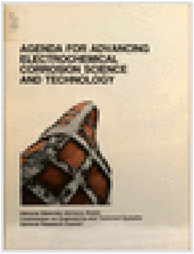

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AGENDA FOR ADVANCING ELECTROCHEMICAL CORROSION SCIENCE AND TECHNOLOGY

Report of the
Panel on Electrochemical Corrosion

Committee on Electrochemical Aspects
of Energy Conservation and Production

National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council (U.S.).

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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ABSTRACT

Corrosion is a pervasive problem; it causes large economic losses, jeopardizes safety, and creates delays in introducing new technology. This report considers the challenges to be faced during the next 20 years and examines the opportunities to develop a comprehensive understanding of corrosion and to use this understanding for corrosion control and avoidance. The major technical discussion in the report addresses these opportunities in three general areas: corrosion research and engineering, advanced materials, and information dissemination. Benefits to key transportation, infrastructure, and energy sectors that would result from a comprehensive systems analysis approach to corrosion science and engineering are also noted. This study makes recommendations for a new approach to corrosion science and technology in a framework of six central issues: theory and modeling, experimental probes, lifetime prediction, advanced materials, multidisciplinary efforts, and education.

On the cover: A section of the "flame" on the Statue of Liberty's torch before restoration. This flame, with its colored glass inserts supported by copper attached with iron fasteners to a supporting iron armature bar structure, was a 1916 modification by sculptor Gutzon Borglum of Bartholdi's original design. The section shown is approximately 5 feet high. Corrosion was responsible for much of the deterioration that took place during the Statue's first 90-plus years. The galvanic corrosion of the fasteners shown in the cover photo is only one symptom; water leakage also severely corroded the iron armature inside. After its 1986 restoration, the flame consists of copper covered with gold leaf applied using a repoussé technique. (Photo courtesy of Robert Baboian, Texas Instruments, Inc., Attleboro, Massachusetts)

PREFACE

Electrochemical corrosion exacts an enormous toll on the U.S. industrial base and its economy, representing losses on an annual basis of approximately 4 percent of the gross national product. Corrosion can be a limiting factor in the development of new technologies and engineering systems, particularly where sufficiently corrosion-resistant materials are simply not available. The performance of complex engineering systems may be compromised by the lack of chemically stable materials for critical components. Likewise, as more advanced engineering systems employing new, high-performance materials are designed, corrosion resistance may become a critical issue.

The field of corrosion science and engineering has high economic leverage. This field (as with the fields of fracture, wear, and other forms of deterioration) is a problem-solving rather than product-oriented discipline. It contributes to the success of other technologies and, as such, is not accounted for directly in the competitiveness of the industrial base in the United States. It represents an element of the technological infrastructure required to sustain the nation's defense and its industrial and economic well-being. It is intrinsic to the nation's competitive success through both product improvement and reduced maintenance costs for the public and private infrastructure.

The Panel on Electrochemical Corrosion was formed to review technical problems and identify research and development opportunities in this field. The panel acted as a subgroup of the Committee on Electrochemical Aspects of Energy Conservation and Production. This committee was convened by the National Materials Advisory Board in response to a request from the Office of Conservation and Renewable Energy of the Department of Energy that the National Research Council assess electrochemical science and technology relevant to energy and materials conservation. Readers interested in this broader subject are referred to the committee's report (NMAB 438-1, *New Horizons in Electrochemical Science and Technology*).

The approach taken by the panel in this report was to identify directions for an improved science and technology base for corrosion and corrosion control. This base would assuredly lead to energy and materials conservation through improved design of engineering systems and improved specification of materials. This report argues that there is a substantial difference between perception and reality in corrosion science and engineering. Although the perception may exist that this field is unlikely to affect the vitality of the industrial base, the reality is that materials degradation imposes a significant cost on the economy and influences the ability to introduce new technologies and to take full advantage of contemporary engineering concepts. Recommendations central to advancing the field are given in Chapter 1 of this report. Chapters 2 and 3 discuss, respectively, general introductory issues and the impact of corrosion in major areas of society. Detailed discussion supporting the panel's recommendations is given in Chapters 4 through 6.

The principal audience for this report is the technical community active in corrosion science and engineering and managers of research and development in this field.

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California, provided original material on corrosion on phosphoric acid fuel cell systems.

David A. Shores, Corrosion Research Center and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, provided original material on hot salt corrosion and corrosion in molten carbonate fuel cells.

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Chapter 1

EXECUTIVE SUMMARY

Corrosion is the process of uncontrolled chemical or electrochemical attack of a material by species in its environment leading to degradation of its original properties. In one form or another, electrochemical corrosion has been documented in metals, alloys, semiconductors, ceramics, glasses, polymers, and composites—that is, in all classes of materials. Although much progress in corrosion control has been made, major problems remain. The impact of corrosion on society is significant in terms of personal injuries, actual economic costs, and unrealized new technologies; this issue is addressed in Chapter 3 with respect to benefits that would accrue to key transportation, infrastructure, and energy sectors from a comprehensive systems analysis approach to corrosion science and engineering.

This study was undertaken to review technical problems and identify research opportunities in corrosion science and engineering. It concludes that current approaches to corrosion prevention and control, based on narrowly focused problem-solving, on development through enlightened empiricism, and on generally unsystematic application of existing knowledge, are inadequate for meeting present and future needs. The study also concludes that there are opportunities to develop a more effective approach to corrosion control because of (a) recent gains in computational capabilities, (b) new measurement techniques, and (c) conceptual and experimental developments in other fields that are relevant to corrosion. *Thus the field of corrosion science and engineering is at a transition toward a greater dependence on scientific rigor and away from empirical methodologies.*

To reduce and control corrosion, the goals are clear: the development of surfaces engineered to be stable against corrosion and the application of existing and new technology to minimize corrosion in the service environment. The opportunities are challenging. To a large extent the elements needed to take advantage of them are already in existence. The required capabilities are becoming available in the scientific ability to model surfaces and interfaces, in the computational facilities for modeling, in the electrochemical and surface science techniques for studying interfaces in situ, in the materials technology for the production of designed surfaces and materials, and in the educated scientists and engineers who can perform these tasks.

The opportunities have both technical and institutional aspects that are reflected throughout this report, *with a recurrent emphasis on the* *multidisciplinary nature of the field of corrosion science and engineering.*

The subsequent chapters address these opportunities in three general areas: The first is electrochemical corrosion science and engineering (Chapter 4), which focuses on measurements of corrosion, on the fundamental understanding of corrosion processes, and on the utilization of measurements and understanding in the engineering analysis of corrosion systems and in the prediction of useful life. The second area is corrosion research on advanced materials (Chapter 5), which includes several selected topics in which improved and new corrosion control technologies, based on fundamental understanding and systems analysis, are needed. The third area is dissemination of corrosion information (Chapter 6), which examines transmittal of information on corrosion and corrosion control to the users of materials.

An approach that builds on existing multidisciplinary capabilities of individuals and institutions is required. Further, this approach must provide a mechanism that integrates multidisciplinary activities into a framework that brings coherence to complex phenomena and yields a comprehensive basis for understanding them. The approach proposed here addresses these requirements through six central recommendations, which cover theory and modeling, experimental probes, lifetime prediction, investigation of advanced materials, multidisciplinary efforts, and education. The framework provided by these recommendations offers (a) guidance for research on corrosion, (b) strategies for dealing with corrosion of advanced materials, (c) support for improvements in the design of structures and equipment with increased corrosion resistance, and (d) approaches to determining operating conditions for components to minimize or prevent corrosion-induced failure.

The six recommendations are as follows:

- **Theory and Modeling:** *Greater emphasis on modeling and theory is recommended for both elementary corrosion processes and their interactions in complex macroscopic systems. Given the opportunities and need in the next decade for corrosion science and engineering to adopt advances in other disciplines, the panel endorses greater support of theory and modeling, even if the total support for corrosion research remains constant.*

Two complementary areas for theory and modeling are identified in Chapter 4—elementary processes and macroscopic systems. Regarding elementary processes, new theoretical approaches for characterizing electrolytes are in hand and are being applied to dielectric-solvent interfaces. Just emerging are theoretical treatments for the physics of electrons at metal-electrolyte interfaces. The incorporation of understanding from both these areas in theories to describe the elementary processes at metal-electrolyte interfaces is possible, even for the complex interfaces encountered in corrosion systems. Extension of this work to include interfacial films will provide a fundamental physical understanding of metallic corrosion capable of predicting corrosion behavior from first principles.

Descriptions of individual corrosion processes can be assembled and used to predict materials degradation in macroscopic systems. However, the necessary computations are usually so lengthy and complex as to require access to large-scale computational facilities. Expansion of this approach to the analysis and prediction of corrosion behavior on a wider scale requires the development of more efficient mathematical techniques and algorithms and of methods for simplifying the calculations without loss of significant factors.

- **In Situ and High-Resolution Experimental Probes:** *The active support now given to the development of probes to measure corrosion processes in situ and with the spatial resolution needed for studying local corrosion phenomena should be continued. Of particular urgency is the use of probes wherever possible as sensors for on-line monitoring of corrosion of components in technologically important systems.*

Over the past decade, a revolution has occurred in the field of electrochemistry with the development of in situ and ex situ surface analysis techniques capable of resolving important phenomena on both microscopic and short time scales. These techniques should be adapted and utilized to characterize local physicochemical corrosion events in situ. In addition, in situ techniques should be extended to provide on-line monitoring of real-world systems where reliability often requires detecting the onset and progress of corrosion phenomena (e.g., induction time and propagation rate for pitting or cracking). These issues are amplified in Chapter 4.

- **Lifetime Prediction in System Applications:** *Increased attention should be devoted to developing quantitative methodologies for predicting lifetimes that couple advanced models with identification and measurement of critical parameters and with computer-based expert systems. This effort will necessitate generating physicochemical data bases to support systems analysis as well as using advances in theory and experimental techniques discussed earlier.*

A major objective of corrosion science and engineering is to permit the selection of materials to give corrosion resistance compatible with system design in specific service environments. Even for the simplest case—general corrosion of metals—present lifetime prediction strategies are qualitative or nonexistent because of the lack of (a) realistic models, (b) understanding of critical parameters, (c) test data, or (d) suitable coupling between the models and the experimental results.

These factors must be addressed if materials are to be selected for reliable and economic service. In addition, these methodologies must be incorporated into a technological framework usable by designers who do not have detailed knowledge of corrosion.

Currently available thermodynamic and kinetic data bases (see Chapter 4) are too incomplete to support quantitative modeling of many corrosion systems, particularly those where predictions of corrosion behavior under extreme conditions or over extended periods of time are desired. Because the unavailability of data limits the use of models, a critical need exists to upgrade and expand the sources of information on the thermodynamic properties of chemical species, kinetic exchange current densities, activity coefficients, rate constants, diffusion coefficients, and transport numbers, particularly where concentrated electrolytes under extreme conditions are involved. Many of these data are obtained in disciplines that traditionally have been on the periphery of corrosion science, so it will be necessary to encourage interdisciplinary collaboration to meet the need.

A number of proprietary expert systems (see Chapter 6) are being developed for corrosion engineering, specifically for materials selection in marine environments, in pressurized water reactor steam generators, and for high-strength aluminum alloys. The availability of computer-based expert systems for corrosion engineering will improve the performance and reliability of new structures operating in the domains of applicability of these systems. Knowledge of corrosion and corrosion-related phenomena for the specific materials under consideration for use is an important input to the materials selection process in the early stages of design, where problems can be dealt with most effectively and without compromising design intent. This knowledge is at present gained principally through practical experience and thus is held by "experts." Codifying their knowledge for wider accessibility and utility will lead to improved corrosion-resistant designs.

- **Corrosion Resistance of Advanced Materials:** *The corrosion behavior and limits of chemical stability of newly developed materials must be determined as an integral part of materials development in order to indicate where more detailed modeling and experimental efforts are warranted.*

In the discussions in Chapter 5 on protective surface phases, ceramics, thin films and electronic, magnetic, and optical materials, composite materials, and metastable alloys, it is noted that the corrosion behavior of new engineering materials and structures must be characterized if they are to be introduced reliably into technology. These characterizations should establish the limits of corrosion resistance in the relevant service environments and show where more detailed study is needed. With many advanced materials, technological applications depend on the existence of properties other than corrosion resistance, and the understanding of corrosion phenomena is important in achieving and enhancing reliability while taking advantage of these other material attributes. Too often in present practice, corrosion evaluation comes too late in the development cycle.

- **Multidisciplinary Activities and Education in Corrosion Science and Engineering:** *Opportunities should be explored for industry, government, and academia to foster multidisciplinary research approaches. These will draw on advances made in related fields of physics, mathematics, and electrochemistry, among others, and build on the strengths of individual participants and facilities in these several fields.*

Advances in the stabilization of interfaces will benefit from enhanced multidisciplinary approaches in education, in research, and in application. Because corrosion science incorporates elements of physics, chemistry, electrochemistry, materials science, mathematics, and engineering, it is essential that scientists and engineers skilled in these disciplines be encouraged to contribute to this field—to its concepts and theories, predictive methods, and experimental techniques. The panel concludes that industry and government should provide this encouragement by expanding support of collaborative efforts. The panel further concludes that an essential part of the development of this field will be improved undergraduate and graduate education in universities; this is needed to provide trained engineers and scientists capable of contributing to advances called for in efforts recommended in this report. Further discussion is given in Chapter 6.

- **Instruction in Corrosion Practice:** *Improved education must be provided on a continuing basis to engineers responsible for materials selection.*

As discussed in Chapter 6, a broader knowledge of corrosion on the part of the users of materials in design will result in major reductions in the corrosion-related costs of maintenance, repair, and replacement. The correct selection and use of materials to withstand the corrosive environmental influences that cause degradation and failure must be based on an appreciation of factors causing and controlling corrosion and the ways in which they can affect materials and structures. Improved transfer of corrosion control technology into system design will require greater knowledge of these factors within the design community. Such knowledge can be supplied by utilizing existing resources for continuing education and should be a part of the background of all those who are concerned with design. However, the education of engineers with respect to corrosion at the bachelor's level is deemed inadequate; their curriculum will probably be limited to a single course on materials. Efforts should be made to include more laboratory experience in corrosion in conjunction with lecture courses at this level.

Chapter 2

INTRODUCTION

Rarely are materials stable in their service environments. This instability is inherent; the thermodynamic forces responsible for it are fundamental in nature. One result of this instability is corrosion, the chemical breakdown of materials with the loss of useful properties. Depending on the circumstances, corrosion occurs slowly or rapidly, uniformly or locally, continuously or abruptly. In one form or another, it has been documented for metals, alloys, semiconductors, ceramics, glasses, and polymers—that is, for all types of materials.

Except where a material is stable or is stabilized through the application of protective technology in its service environment, corrosion eventually occurs and may lead to material and component failure. This may determine the useful life of the structure of which the material is a part. More typically, it establishes requirements for maintenance and repair of automobiles, aircraft, ships, bridges, chemical processing plants, electric power generation stations, equipment, and other facilities. Replacement, maintenance, and repair and the time spent to accomplish them constitute a major part of the nation's cost of corrosion. When these issues are slighted, when they are inadequate to the task, and when they are not recognized as a part of the materials selection process, materials fail, with possibly catastrophic results. For example, bridges collapse (*1*), chemical reactors leak (*2,3*), and radioactive substances escape from nuclear-powered generating systems (*4*). In many such cases, what is required is not so much research and development as effective implementation of known corrosion-control technologies. Although a full understanding of the mechanisms by which failures occur may not be known, corrosion-control paradigms are available to practicing engineers.

Advances in technology depend, to a large extent, on the use of new materials with improved or novel properties and on the use of materials in more severe service environments. In the absence of inherent stability or appropriate technology for stabilization, corrosion may so limit the useful life of a material that desirable advances are precluded. For example, stress corrosion cracking limits the stresses sustainable by available high-strength aluminum alloys in chloride-containing environments; hot corrosion by molten salts limits the operating temperatures for commercial nickel- and cobalt-based superalloys in current gas turbine power generators, the use of ceramics in coal-burning power plants, and the development of molten salt fuel cells for electrical power generation and storage; and hydrogen embrittlement (sulfide stress corrosion cracking) limits the use of high-strength, low-alloy steels in sour gas geoenergy systems. Uncertainty about useful service life of materials can inhibit acceptability of or advances in technology, as in the case of the dependence of the nuclear power industry on the long-term containment of radioactive wastes.

Overall, corrosion has a major impact on the national goals and economy through the costs of maintenance and repair, both for operational continuity and for hazard avoidance, and through the limitations it places on advances in technology. These impacts have long been addressed by workers in the fields of corrosion science and corrosion engineering. Major reviews of materials needs (*5,6*) have placed a high priority on research and development to improve the resistance of materials to corrosion.

Indeed, metallic corrosion represents a major cost to the United States; it was estimated at $70 billion in 1975, about 4 percent of the gross national product (*7*). Of this total, an estimated 15 percent or $10 billion was avoidable, meaning "amenable to reduction by the most economically effective use of presently available corrosion control technology"—that is, the use of the best available corrosion prevention practices in design and maintenance. As a percentage of the gross national product, the avoidable cost of corrosion has not changed significantly in the decade since that report. A second measure of the current lack of success in applying existing knowledge of corrosion engineering to design can be found in the unfortunate number of major problems that have been caused by unanticipated corrosion in nuclear, chemical, and other facilities. In a number of these situations, failures caused by corrosion could be catastrophic in nature, with impacts extending far beyond a local loss of operating function.

Recognizing the importance of this field for the United States and for their individual missions, several federal agencies have maintained ongoing programs in corrosion science and engineering. The funding of these activities for fiscal years 1984 through 1987 was compiled for the Departments of Commerce (National Bureau of Standards), Defense, Energy, and Interior, National Science Foundation, National Aeronautics and Space Administration, and Nuclear Regulatory Commission (*8*). This compilation showed that the *total* federal funding for electrochemical corrosion was about $17 million per year (in current dollars), with slightly more basic research ($9 million) than applied efforts (respectively, type 6.1 in the classification of the Department of Defense versus types 6.2, 6.3, and 6.4). Given inflation in this period (*9*), the funding in constant (1984) dollars decreased by an estimated 10 percent.

Federal support has resulted in substantial progress in corrosion science and technology for exploitation in both government and commercial applications. Benefits have come from (a) the development of new, corrosion-resistant materials, (b) the development of surface treatments and finishes to resist corrosion, and (c) the development of control strategies and technologies to stabilize materials against corrosion in the service environment. The recognized value of this work and the intellectual curiosity and activity it inspires have provided the impetus for expanded education in corrosion science and corrosion engineering. This has led to the growth in the United States of several academic centers with international stature.

Despite much progress, major problems remain. At this time there are substantial opportunities to exploit existing knowledge and technology and to develop new capabilities so that surfaces are designed to be stable against corrosion or to minimize corrosion in the service environment. The opportunities are challenging, with both technical and institutional aspects. The required capabilities are becoming available in the scientific ability to model surfaces and interfaces, in the electrochemical and surface science techniques for studying interfaces in situ, in the computational facilities for modeling, in the materials technology for the production of new materials, and in the educated scientists and engineers who can perform these tasks. The anticipated technical progress in stabilizing interfaces draws heavily on the advances being made in developing concepts, theories, experimental techniques, and systems analysis procedures in such disciplines as chemistry, chemical engineering, mathematics, mechanics, metallurgy, and physics. Advances in corrosion science and technology therefore call for improved institutional and collaborative arrangements to facilitate research and development. At the same time, improved institutional and collaborative arrangements are needed to facilitate the transfer and application of corrosion control technology to those concerned with materials in design and in the service environment. The need for multidisciplinary activities constitutes one of the principal themes of this report.

A second theme is the need for continuity, both in support and in direction, in the funding of work in corrosion science and corrosion engineering. The multidisciplinary research and development that are necessary to understand and overcome the surface instabilities that result in corrosion and the multidisciplinary applications of this understanding to corrosion control technology are long-range efforts and will lead to benefits that will expand over the next 5 to 20 years. To be successful, these efforts must be guided and sustained, in much the same way that work based on the disciplines of biochemistry, chemistry, genetics, and physiology is maintained in support of preventive medicine.

Because of the complex and interrelated nature of corrosion phenomena, this report emphasizes generic issues rather than concentrating on each specific form of corrosion. The latter approach has been taken in other studies; for example, numerous reports can be found on the importance of stress corrosion cracking or of understanding the role of molybdenum additions in affecting the pitting resistance of austenitic stainless steels (where the state of the art of research is well known and often the subject of major recent conferences).

The emphasis on generic issues is aimed at convincing the reader that advances are needed on issues that are pervasive to all areas of corrosion science. This is well illustrated, for example, by the need to improve the analytical and mathematical skills of corrosion scientists by drawing on advances that have been made in other fields of science and technology. The view is that advances of the kind described in Chapter 4, related to experimental techniques, numerical and systems analysis, and new conceptual approaches, will affect not only understanding of the chemical stability of traditional engineering alloys that have been studied in some cases for decades but also of new materials that are likely to find their way into engineering systems in decades to come.

The individual chapters that follow address opportunities in three general areas:

- Electrochemical corrosion science and engineering (concepts and theories; numerical and systems analysis; experimental techniques; monitoring of corrosion; life prediction and accelerated testing)

- Corrosion research on advanced materials (protective surface phases; ceramics; thin films and electronic, magnetic, and optical materials; composite materials; metastable alloys)

- Dissemination of corrosion information (education in corrosion science and engineering; technology transfer; expert systems for corrosion engineering)

The first of these areas focuses on measurements of corrosion, on the fundamental understanding of corrosion processes, and on the utilization of measurements and understanding in the engineering analysis of corrosion systems and in the prediction of useful life. The second focuses on several selected areas in which improved and new corrosion control technologies, based on fundamental understanding and systems analysis, are needed. The third focuses on the transmittal of information on corrosion and corrosion control to the users of materials.

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Chapter 3

IMPACT OF CORROSION CONTROL: EXAMPLES OF SUCCESSES AND NEEDS

SUMMARY

Substantial economic leverage is gained from advances in corrosion science and engineering (*1*) that lead to reduced interruptions in the operation of plants and equipment as well as to the commercialization of new products, improvements in public safety, and promotion of new technologies and perhaps new industries. The first two factors contribute to the vitality of existing technology in specific sectors of the economy, and all underline the importance to the national interest of focused support of corrosion science and engineering.

Corrosion control is critical to the economic viability and the technical feasibility of engineering systems that significantly affect society. Corrosion problems and their control in three sectors of society (automobiles, infrastructure, and energy systems) are discussed, with emphasis on the successful implementation of corrosion control methods. In two of the systems described in this chapter—automobiles and infrastructure—the emphasis is on present technology; improved access to this is essential. The third area addressed is energy systems; many of these may not be commercialized unless means are found to reduce corrosion degradation below the level achieved by present control methodologies.

The costs of corrosion of automobiles are recognized by the general public. For infrastructure and energy systems, the costs and design penalties imposed by corrosion are known principally to specialists, yet these govern successful implementation of many new technologies. In the latter category should be noted the economically important solutions of zirconium alloy nuclear fuel cladding problems and solutions related to corrosion, stress corrosion cracking, and hydrogen embrittlement. Discussion of these areas where progress has been made calls attention to both the strength of present technologies and the need for long-term corrosion research based on a systematic and comprehensive approach, as discussed in subsequent chapters of this report.

AUTOMOBILES—A MATURE APPLICATION NEARING SUCCESS

Corrosion of the personal automobile in the United States has increased in the past 3 decades, primarily because of the increased use of salt on winter roads to aid in snow and ice removal. The recoverable cost of corrosion of automobiles is estimated (within a factor of two) to be \$15 billion per year (*2*) or, on average, \$100 per year per automobile. This is the recoverable or avoidable cost that could be realized by prevention and control. The cost results from the increased capital investment required for excess capacity and redundant equipment, maintenance and repair, corrosion prevention, design, loss of product, technical support, insurance, and increased parts and equipment inventory.

In response to consumer (market-driven) forces, the automotive industry has made a commitment to corrosion-control technology. An industry goal is the 5- to 10-year standard for corrosion control—i.e., 5 years for no perceptible corrosion (no change of appearance caused by corrosion) and 10 years with no perforation of body panels caused by corrosive attack. This goal has focused attention on four issues:

- Improved quality control to minimize defects
- Improved materials selection to reduce susceptibility
- Improved design
- Development of advanced materials, including tougher, more durable coatings and paints

The first three issues require improvements in technology transfer based on present knowledge. Better technology transfer through continuing education of designers is a major need. This would result in improved materials selection and improved mechanical design—for example, to avoid crevices, which are natural sites for enhanced attack. In addition, the advent of expert systems for corrosion engineering will be useful for the designer, especially if utilized as part of a systems approach to design. The fourth issue is identified because most corrosion problems on automobiles start at defects or damage areas in surface coatings and paints and spread as the coating delaminates in adjacent areas. Corrosion is also seen in areas where electrolyte is trapped in crevices and recesses on the inside of the body panels. Other corrosion may occur in the mechanical support, fuel delivery, and electronic systems of vehicles.

Areas for research and development of new technology over the next 2 decades include the following:

1. Electrogalvanizing. Investments by automakers and six steel companies in five new electrogalvanizing lines amount to over \$500 million (*3*). These lines produce roll-coated stock used for auto body panels. Both zinc and zinc alloys are used for the coatings, and the substrate is high-strength steel. Ordinary hot-dip galvanizing lines can be used for some processing, but high-strength steel cannot be processed

in this way because of tempering effects at the bath temperatures. The introduction of galvanized steel has required the development of new paints and surface treatments to replace those that have been used for processing ordinary steel surfaces. Other problems have been encountered, such as forming the sheet stock without delaminating the zinc coating, welding the coated material, and deforming or cracking the coating.

2. Other types of surface processing. Electrophoretic coatings, ion implantation, laser surface alloying, clad coatings, sprayed metal coatings, vapor-deposited coatings, conversion coatings, organic coatings, petroleum-based rust preventives, and sealers are some of the methods that deserve consideration. Physical parameters of coatings such as permeability, porosity, and adhesion will receive greater attention as more is learned about the mechanisms of failure. The chemistry and physics of the relevant interfaces must be studied with more spatial and time resolution to reveal the details of failure processes.

3. Improvements in accelerated testing and simulation. Major benefits would accrue from increased lifetimes of automobiles in service and better predictability of that lifetime. At present, accelerated tests of corrosion resistance are unsatisfactory because they do not adequately simulate a corrosion system over the full time scale desired, nor do they adequately simulate conditions expected in the field. Improved methodologies may result from better understanding of the failure mechanisms and their correlation with fundamental processes at and near the corroding interfaces. Simulation and modeling will contribute to the development of accelerated testing, and vice versa.

4. New and advanced materials. New alloys and polymers for body parts and coatings are being sought for improved corrosion resistance and lower costs. Past materials developments have had significant favorable effects on automobile corrosion control. As the new materials are introduced, it will be important to develop methods of joining that will not introduce galvanic effects or other forms of corrosion.

5. Inhibition of paint degradation. A major cause of corrosion initiation in automobile bodies is the photolytic degradation of paint ("chalking"), which leads to penetration of water and oxygen through the protective coating to the steel surface. Methods need to be developed to prevent electron "holes" generated photolytically in the TiO_2 pigment from oxidizing the surrounding polymer (paint) matrix, possibly by encapsulating the pigment particles in an inert polymeric sheath or by using a different (wider band gap) pigment.

INFRASTRUCTURE—A PROBLEM OF GROWING SIGNIFICANCE

The national infrastructure includes public works such as highway systems (pavements, bridges, tunnels); water and wastewater distribution, collection, and treatment systems (pipelines, culverts); and transportation facilities (port and harbor structures, locks, dams, reservoirs, railway and subway lines) (*2,4,5*).

The primary electrochemical issue regarding infrastructure materials is the control of the corrosion of steel in a wide range of environments and construction applications. This primary issue is further divided into two classifications:

1. Control of the corrosion of reinforcing steel embedded in concrete. The primary challenge for corrosion science and engineering in relation to the infrastructure is the corrosion of reinforcing steel in concrete. This problem resulted from an unanticipated change in that environment. Before the late 1960s, very little deicing salt was used in the United States, as there was not a public demand for "bare pavements" in the wintertime. Protecting the reinforcing steel in concrete bridges against chloride-induced corrosion was therefore not a concern. With the introduction of deicing salts, a marked increase of corrosion resulted, and the structures began to deteriorate. This problem has become severe, and efforts have been marshalled to reduce the degradation. Notable successes have been made—for example, polymeric and other coatings for rebar steel and the development of less permeable concrete (*6,7*). In the latter, microsilica modifications of concrete have been shown to be 10 to 100 times less permeable than the base materials. Other advances include cathodic protection of steel imbedded in concrete roadways, and weathering steels have shown improved resistance to attack in bridges and other applications. Nevertheless, the problems that remain are enormous, and a recent report estimates the cost of replacement and refurbishment of infrastructure facilities to be billions of dollars (*8*).

Some of the research that remains to be done pertains directly to the concrete as the medium in which moisture, oxygen, hydroxyl groups, and chloride ions are transported. In addition to transport of the aggressive environment to the metal, the electrical resistivity of the concrete may determine the success of cathodic protection or the distribution of attack caused by stray currents. Additional progress in corrosion control is needed in three areas: diagnostic and in situ tests, developing restorative procedures, and developing means of building more durable facilities. Technology is currently available that could have prevented many of the problems now existing in the field. Technology transfer is therefore considered to be particularly important; development of computerized expert systems and materials performance data bases could help provide access to the necessary corrosion control technology. Unfortunately, many of the problems cannot now be corrected unless progress is made in post-treatment of concrete (*8*); most information on this treatment appears to be proprietary but probably addresses the reduction of the permeability of concrete to moisture.

2. Control of the corrosion of steel structures in which the steel is directly exposed to the corrosive environment. The importance of steel corrosion in buildings, bridges, pipelines, underground storage tanks, and offshore structures is generally understood. The phenomena of aqueous corrosion in fresh, salt, and polluted waters, of atmospheric corrosion in clean and polluted air, including the effects of acid rain, and of stray currents are familiar to corrosion specialists (*9*) and, except in special cases, do not represent new research opportunities in electrochemistry. Many failure analyses cite crevice corrosion, anodic fasteners, and the inadvertent creation of electrochemical cells as the reasons for the observed deterioration. The solutions to such problems require, instead of further research, the establishment of multidisciplinary teams to bring appropriate technology to bear during the design phases of such facilities. Computerized data bases and expert systems to aid the design engineer are required. Designs that are poor from a corrosion standpoint could be minimized if those responsible for design had adequate training in corrosion prevention. Research on mechanistic fracture models, particularly for sections of components having gradients in composition or microstructure, such as weldments, would provide capabilities useful for facilities management, as would development of sensors and life-prediction models.

NEW ENERGY TECHNOLOGY SYSTEMS—A COMPLEX ISSUE INVOLVING RELIABILITY AND ECONOMICS

Substantial corrosion problems exist in energy conversion systems. These have been addressed (*10,11*) for low-temperature aqueous systems and for high-temperature systems. Critical problems of localized corrosion remain to be solved in these systems, despite continued efforts. These problems include, for example, stress corrosion cracking and corrosion fatigue of structural components in light-water reactors (*12*) and other energy sectors and cyclic fatigue damage on offshore oil and gas structures (*13,14,15*). In the latter application, welded carbon steels, used extensively in fixed platforms and mobile rigs, must be designed for 30- to 40-year life, a formidable challenge considering the size of the welded structures and the complex metallurgical, mechanical, and environmental variables that affect their behavior. Deeper oil and gas wells involving aggressive environments and new tethered structures requiring higher strength steels may exacerbate environmental failures. In high-temperature systems, corrosive thin films of salts and slags attack the metals used in gas turbines, heat exchangers, fuel cells, and batteries and cause premature failure.

Many of these same forms of corrosive attack affect other technologies as well; crevice corrosion, for example, may be more important in specific areas, such as the chemical process industry. It is important to identify failure modes that are peculiar to individual energy technologies, but it is also essential to detect and monitor the onset of the localized attack. As discussed in Chapter 4, the development of monitors for corrosion is required to assist life prediction of materials and structures. Coupling monitors and detectors with mechanistic models of attack permits enhanced control and management of the attack in structural components. The benefits of the comprehensive approach are improved design, optimization of materials and facilities utilization, life extension and prediction of affected components, and optimization of inspection intervals. The safe and economic operation of energy systems is thereby facilitated.

In the following sections, several examples of new energy technology systems are discussed. The impact of corrosion problems is identified, and then some recommendations for controlling the degradation are made. The recommendations are made, however, in the context of the chapters that follow, where the generic issues facing corrosion control and prevention are discussed.

Solar Thermal Systems

Mirrored surfaces play an essential role in solar thermal energy applications (*16*). An ideal solar reflector would retain high optical performance with low initial cost and no maintenance over the long design lifetime (decades) of the system. Reflectors will be multilayered—a thin film of paint over copper over silver on a glass (or polymer) substrate. Electrochemical corrosion during service is a major concern. Corrosion at the copper-paint interface appears to result principally from water permeation through the paint, leaching chloride ions from the paint itself and forming copper chloride; copper sulfide (the sulfur coming from the atmosphere) has also been reported as a corrosion product. Silver oxide and sulfide also form in moist environments, the oxidation being enhanced by photo-stimulation and leading to pinhole formation in the silver film and concurrent loss of mirror reflectance.

Advances in both corrosion science and engineering are prerequisites for reliable commercialization of mirror technology for solar thermal systems. For example, the role of atmospheric contaminants and corrodents and impurities in paints needs to be determined. At the fundamental level, mechanisms for oxidation-reduction reactions and methods for their inhibition need to be established. On the engineering level, reaction rates need to be tabulated, and standardized accelerated tests must be sought.

Photovoltaic Solar Energy

In photovoltaic modules, the system parameters include (a) the materials used for the solar cell (amorphous Si, polycrystalline Si, GaAs, CuIn-Se, CdS, etc.), the electrical contact metallization (Cu, Ag, Ag-Ti, Cu-Be), the (polymeric) encapsulant, and the antireflection coating, and (b) the exposure of the modules to terrestrial conditions of ultraviolet rays, heat, diurnal cycles, and atmospheric gases (H_2O, O_2, NO_x, CO, etc.). The major potential problem in photovoltaic modules is electrochemical corrosion at the interfaces involving the semiconductors, the metallization, the encapsulant (polymeric), and the antireflection coating (*17*). Accumulation of a few monolayers of water at an interface in the multilayer structure can establish an electrochemical corrosion cell that may lead to degradation in cell performance. Photo-enhanced corrosion and photo-enhanced catalytic effects may also result in degradation of the cell performance and lifetime.

Research is needed to determine both the generic mechanisms of electrochemical and photo-assisted electrochemical corrosion and the specific corrosion of candidate cell materials in real environments. Materials combinations that will reduce the potential for corrosion to occur at interfaces in photovoltaic modules also need to be identified.

In a related area, photoelectrochemical systems (*18-21*), research is needed to understand (a) the photocorrosion processes at semiconductor-liquid interfaces in more detail, (b) detailed mechanisms of charge transfer at semiconductor-liquid interfaces, and (c) corrosion suppression effects of modified surfaces.

Sodium-Sulfur Battery

The sodium-sulfur battery has a coaxial configuration of an outer steel can, a molten sodium polysulfide electrode, a beta alumina electrolyte, and a molten sodium electrode. Electrochemical corrosion of the can, part of the electrical current collecting system, is a major problem (*22,23*). Cost considerations limit the can to inexpensive commercial alloys, usually chromium-plated or chromized mild steel. The chromium plate forms an adherent passivating chromium sulfide layer in the polysulfide electrode, but pits form in this layer. The chromized steel forms a chromium carbide layer during the vapor deposition process that is also adherent and passivating, but it cracks upon cooling. At both types of defects, corrosion of underlying steel occurs with two deleterious results: The first is a compromised structural integrity of the can; the second is iron contamination of the electrolyte. It is hypothesized that the iron occupies sodium sites in the electrolyte and reduces its ionic conductivity.

Both basic and applied research are needed to improve corrosion control in this cell—e.g., to determine the origin of flaws in the chromium plate and the potential of different coatings on the steel, such as Mo, Ce and CeS, TiN, SrO, and Ru_xS_y. More fundamental studies of the effect of impurity contamination on conductivity in the electrolyte are warranted.

Fuel Cells

Fuel cells offer potentially significant efficiency and cost advantages for electrical power generation. As currently conceived, molten carbonate fuel cells are constructed in a flat, square-plate sandwich arrangement. The central or core layer is molten carbonate contained in the pores of a loose agglomeration of $LiAlO_2$ (called the "tile"). In contact with either side of the tile are porous electrodes—the anode, typically of Ni, and the cathode of NiO incorporating dissolved Li. In contact with each electrode is a current collector, usually of stainless steel, which also serves as a duct for passing gases over the electrode. There are at least three important high-temperature corrosion problems (*24-27*): (a) degradation of the NiO cathode, (b) hot corrosion of the bipolar current collector-separator plates, and (c) hot corrosion of the gas seals between the tile and the cell housing.

Phosphoric acid fuel cells at present use hydrogen directly. In the fundamental electrochemistry occurring in the electrochemical energy conversion subsystem, protons produced at the anode are transported via the acid electrolyte to the cathode (air electrode), where they react with oxygen to form water. The product water is transported from the cell via transpiration to the reactant air stream. In current technology, the anode catalyst is platinum supported on conductive carbon black. The cathode catalyst is typically platinum supported on a graphitic carbon (e.g., a graphitized furnace-processed carbon black). Within a cell, anode and cathode are separated by a SiC powder matrix soaked with phosphoric acid. The operating conditions are typically 190 to 210°C, 95 to 99 percent acid, and, in pressurized versions, 50 to 120 psig total pressure; acceptable lifetime is currently defined as at least 60,000 hours of operational time. Corrosion processes occur primarily at the cathode, in the catalyst layer, and in the electrode substrate layer (*28,29*). These processes affect lifetime by forming dendrites that short-out the cell, and they limit cell voltage by stripping the platinum from the cathode. Although platinum dissolution limits the maximum achievable cell efficiency, little is known about its dissolution in phosphoric acid. A more corrosion-resistant support material would also be desirable, although it is not clear what new class of conducting materials will be found.

Geoenergy Systems

Geoenergy systems (oil and gas wells, geothermal reservoirs, geopressured resources) frequently involve aggressive environments (e.g., brines) at high temperatures and pressures. Corrosion is a major factor (*30-33*) involving, for example, hydrogen embrittlement of carbon steels in near-surface and above-ground systems, while erosion-corrosion, pitting corrosion, and chloride effects on stainless steels are relevant to the deeper portions of wells. Polythionic acid cracking of sensitized austenitic stainless steels similar to that in oil refineries is a continuing problem. More sophisticated methods—e.g., sensors and monitors—are needed for detecting and characterizing the nature of the corrosive attack in remote downhole locations. For example, oil and gas cannot be produced from very deep wells because current Fe-Ni-Cr-Mo alloys are not resistant to the aggressive brine environments (*34-37*).

Advances must be made in defining the composition of the corrosive environments. Also required are an improved understanding of various failure mechanisms, a greatly expanded data base for the behavior of materials in these extreme environments, and the development of improved empirical and theoretical correlations for predicting service life.

Nuclear Power Generation and Waste Containment

In nuclear power plants, the loss of plant availability (the capacity factor loss) costs about $1 billion annually, and much of this is directly attributable to localized corrosion of the structural metals exposed to the hot-water environments. In boiling-water reactors, stress corrosion cracking of recirculation lines (*38*) is a significant problem, whereas in pressurized-water reactors the more serious corrosion problems arise in the steam generators and are identified as denting, intergranular attack, tube pitting, and tube cracking (*39-41*). Some opportunities remain for research and development, but, more importantly, successes reported show how long-term corrosion research on complex systems problems can lead to economically important solutions (*42-45*). The monograph by Roberts (*42*) may be consulted for a more comprehensive discussion of nuclear plant materials and design considerations. In spite of substantial prior research, important needs and opportunities exist in selected areas: the kinetics of electrochemical redox reactions on metal surfaces in hot water systems, the formation and disruption of passive layers in high-temperature water, and the development of new monitoring techniques and methods.

Under current proposals for nuclear waste containment, the radioactive waste package must be contained in the repository without leakage of radioactivity into the environment for a period of 1000 years. For structural integrity of the waste package to be assured, a valid predictive capability must be developed based on understanding of the processes that occur, their time dependence, and the system response to these. Relevant existing test data will need to be extrapolated 3 to 5 orders of magnitude in time for a containment system subjected to a complex environment involving highly concentrated aqueous solutions, temperatures in excess of 100°C, radioactivity, and a heterogeneous geologic structure (either salt, basalt, volcanic tuff, or granite). The most important needs are (*46-49*) (a) a better generic understanding of how solution chemistry can alter the corrosion products formed on mild steel (a reasonably passive magnetite film forms in high-sodium brines, but a gel-like nonpassivating magnesium-ferrous hydroxide forms in high-magnesium brines); (b) an expanded data base of information on the compositional effects of aqueous solutions on the corrosion of proposed container materials along with an assessment of the quality of the data and their statistical reliability; (c) the design of accelerated corrosion tests; and (d) an understanding of variability and changes in the container metallurgy (especially at weldments).

Superconductor Materials

The recent development of high-temperature superconductors (e.g., perovskites such as $YBaCu_2O_{4-x}$) has opened up exciting possibilities in energy transmission and data processing. However, it appears that these materials are attacked by components of ambient atmospheres. Indeed, some recent work has shown that interaction of ceramic $YBaCu_2O_{4-x}$ superconductor materials with water vapor causes deterioration of the ohmic contact between the metallic current collector and the superconductor substrate. Products such as $Cu(OH)_2$ and $Ba(OH)_2$ build up at the interface, and depletion of yttrium occurs. At present, very little is known about this important corrosion process, but it appears likely that environmentally induced degradation will become a critical issue in superconductor technology.

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Chapter 4

ADVANCES IN ELECTROCHEMICAL CORROSION SCIENCE AND ENGINEERING

SUMMARY

The overall goal of this report is to identify opportunities to develop a new approach to the field of corrosion science and technology over the next 2 decades. This chapter focuses on opportunities in modeling and experimentation irrespective of specific material or application. Some opportunities exist because of recent capabilities developed in other areas—new electrochemical and other localized probes, new concepts and theories of the physics and chemistry of the interface region, and new computational facilities for modeling. Other opportunities arise because of the large data base now available on the corrosion of conventional alloy systems—a data base often expressed as empirical correlations and relationships or as engineering rules of thumb. Research needs and directions are discussed in this chapter for the following:

- Concepts and theories: Advances are required on two levels—a microscopic basis, where the fundamental physics and chemistry of the solid-liquid interface must be formulated and understood locally, and on a macroscopic level, where interaction of these local regions on a heterogeneous surface must be addressed.

- Numerical and systems analyses: Suitable coupling is needed of the existing capability for quantitative modeling of the transport in electrolytic media, including multicomponent systems with varying pressure and temperature, and experimentation on time and length scales that are appropriate for the phenomena; additional encouragement should be provided for developing this comprehensive systems approach to corrosion science and engineering.

- Experimental techniques: New techniques, many of them deriving from the field of surface science, offer greatly enhanced observational capabilities, in some instances at the level of atomistic detail at interfaces in condensed media.

- Monitoring: New and present laboratory experimental techniques need to be applied to the more complex and often more extreme field conditions where monitoring is required.

- Life prediction and accelerated testing: Considerable progress has been made recently in the development of life prediction models based on

fundamental mechanisms that provide quantitative relationships between material tests and long-term component performance. With continuing advances in theory and in systems analysis, this mechanism-based methodology can ultimately be extended to predict lifetimes relevant to most types of corrosion, a major advancement in technology.

CONCEPTS AND THEORIES

Corrosion science dates back to the early part of the nineteenth century with the pioneering work of Faraday (*1*) on passivity. Since that time, advances in understanding corrosion processes have stemmed either from general developments in such areas of science and technology as physics, chemistry, and metallurgy or from highly specific needs to extend understanding of particular corrosion reactions. Thus, Wagner and Traud's (*2*) electrochemical theory for corrosion followed from the classic work carried out by Tafel, Butler, and Volmer in electrochemistry to understand the relationship between current and voltage. On the other hand, the film rupture theory for stress corrosion cracking was developed to explain the highly specific nature of crack propagation through austenitic alloys in aqueous environments (*3*). Corrosion science has evolved as a highly interdisciplinary subject and will remain so in the future.

Because of the interdisciplinary nature of corrosion science, many opportunities exist for advancing present theories and for introducing new concepts to explain experimental observations. The challenge facing the corrosion field is not the lack of basic concepts but rather the lack of development of available concepts for application in corrosion science and engineering. The major accomplishments that might be achieved by addressing this problem include

- A more precise understanding of the elementary processes that occur during corrosion

- A greatly enhanced ability to synthesize physical and mathematical models for complex corrosion phenomena that involve many elementary processes of diverse natures

- Transfer of more highly developed concepts and theories to practical corrosion problems

- A much better ability to predict when corrosion reactions will occur and how fast they will proceed, including a much-improved capability to predict "damage functions" for specific corrosion phenomena

- Much-improved theoretical guidance as to what critical experiments should be performed to advance knowledge of materials degradation processes

Research Opportunities

Areas in which it appears that progress can be made are discussed in the following sections. These cover both fundamental aspects that will deepen basic understanding and more specific subjects that relate to particular phenomena.

Physics of the Electrode-Electrolyte Interface

Recent developments in the physics of the electrode-electrolyte interface (*4-6*) have involved both theoretical and experimental studies. The experimental developments will not be considered further here except insofar as they are closely related to the theoretical developments that are of primary interest.

On an atomic scale, a corroding interface must be studied at a level that requires consideration of the quantum mechanics of the electrons in the material. Theories that do this for the vacuum-metal interface and inert metal-solution interfaces (*7,8*) are very highly developed, at least for smooth interfaces. These theories include concepts such as electron tunneling, ion-solvent interaction and relaxation, and the overlap of electron wave functions, and by and large they provide a good conceptual understanding of the physics of charge transfer reactions. However, these concepts have not been applied to the specific case of corrosion, where simultaneous ion transport (anodic ejection of a cation) and electron transport (e.g., cathodic reduction of oxygen) occur. Very recently, several workers have begun to adapt these theoretical developments (*9-14*) to the study of the electrode-electrolyte interface. The results imply significant changes in the existing theoretical picture of the electrostatics of interfaces in the double-layer region. In the near future, these developments can be expected to lead to calculations of the surface electronic structure as the electrode potential is varied. At the same time, calculations can be expected that begin to model the electronic structure of electrodes with surface oxides as well.

To extend these "interface" theories to the case of corrosion, a valid microscopic model of the solvent of the electrolyte is required. It seems very likely that molecular dynamics simulations of the solvent will replace the classical liquid theoretical models—e.g., the mean spherical approximation—that are currently used for these purposes. Several molecular dynamics simulations of the behavior of water at a dielectric interface have appeared (*15,16*). As these methods develop, it will be natural to consider calculating the solvent structure using molecular dynamics techniques while simultaneously calculating the electronic structure of the metal (*17,18*). Models of this kind are absolutely essential for understanding the corrosion behavior of common structural materials such as iron, nickel, chromium, and aluminum alloys.

The end result of this work will be a detailed understanding of interfaces that will support more macroscopic interpretations of corrosion behavior.

Charge Transfer and Chemical Reactions

Significant progress in developing a theory of charge transfer and chemical reaction rates that is applicable to corroding systems can be anticipated on a time scale of 5 to 10 years if sufficient resources are committed to the problem. It will be easiest to describe outer shell reactions, where a reliable description is needed of the solvent-electrode interface and also of the solvated ion participating in the reaction (*19,20*). An additional requirement is a full calculation of the electron transfer process using a refined version of calculations already achieved with very simple models in order to estimate the transfer rates as a function of electrode potential. Such calculations can be expected to yield detailed, realistic results for comparison with experiment. An essential element for modeling these systems is a reliable molecular dynamics model of water that will describe its dissociation as well as its interactions at electrode interfaces. No such model has yet been reported.

Dynamic Processes

Among developments at larger scales, several lines of theoretical development promise to be useful to corrosion research: theories of fractal and dendritic growth, of equilibrium crystallization, and of instabilities in the reaction-diffusion problem.

Two classes of models of the growth of solids from liquids and from vapors under nonequilibrium conditions are now under theoretical study. In one class of models, the structures that develop are highly irregular in shape and can be characterized by a noninteger geometrical dimension (they are thus sometimes called fractals). For example, the diffusion limited aggregation model (*21*) has been successful in accounting for the rate of growth of copper crystals from copper sulfate solution (*22*). It is possible to show that the same model can be used to describe selective dissolution of alloys under some conditions.

A second class of models leads to dendritic growth as, for example, in the growth of metal crystals from the melt under conditions of rapid quench (*23*). Both kinds of models are currently under rapid theoretical development, but the relationship between them has not been fully clarified, and their applications to selective dissolution of alloys, etc., need to be developed.

A related theoretical development is the study of crystallization from the melt at much slower rates, so that the system always remains in quasi-equilibrium. These theories (*24*), which are based on early work of Wulff (*25*), make predictions concerning the shapes of crystals that are grown under equilibrium conditions. It is likely that similar considerations will prove useful in the study of pitting corrosion and in developing a general understanding of phase transformation and charge transfer processes at corroding interfaces.

Finally, it is quite widely recognized in the chemical engineering community that the temporal instabilities that have been extensively studied in the reaction-diffusion problem can be important in electrochemical problems. The circumstances under which these can play a role in corrosion need to be investigated.

Coupled Transport Phenomena

Many corrosion processes involve coupling between fluxes—for example, coupling between the movement of vacancies across a passive film and heat flow in corrosion under heat transfer conditions (*26*). These processes should be examined in terms of the irreversible thermodynamics theories that have been so extensively applied in other areas of chemistry and physics. Onsager's reciprocity relationship provides the quantitative and conceptual links between the separate irreversible phenomena, and, with appropriate experimental results, allows the type and magnitude of the coupling between the fluxes to be defined.

Mechanistic Analysis

Corrosion scientists frequently consider the anodic and cathodic partial reactions to be separate processes occurring on the same surface, when in fact these reactions are often coupled through surface site competition. From a mechanistic and mathematical modeling viewpoint, corrosion processes generally are complex, requiring many intermediates to explain the experimental observations. For example, recent AC impedance spectroscopic studies indicate that at least five adsorbed intermediates are involved in the corrosion of iron in acid solution (*27*).

The development of more efficient mathematical techniques and algorithms for handling complex reaction schemes is needed, both to aid modeling and to guide in selection of critical experiments. These techniques should be interactive in nature, possibly via microcomputers, so that the experimenter can evolve viable mechanisms as more discriminating data become available.

Adsorbed Intermediates and Charge Transfer

Various electrochemical techniques have demonstrated the importance of adsorbed intermediates in electrodissolution (and other) reactions. These intermediates include simple "adions" and surface metal species complexed with the solvent or anions in the system—e.g., $Fe(OH)_{ads}$ and $FeCl_{ads}$. A strong need exists to establish better theoretical treatments of adsorbed species on metal surfaces and to develop experimental techniques that can be used to explore the properties of these species.

The "adion" question in the electrodissolution and electrodeposition of metals has not been adequately resolved. The evidence for these species in the case of simple metals such as Cu and Ag is inferred rather than demonstrated. In more complex, multi-electron systems (e.g., Zn), AC impedance spectroscopy (*28*) has provided strong evidence for the existence of adions. However, there is no clear picture of the electronic structure of adions or how they interact with the bands in the underlying metal. Also, adequate theories and concepts are not currently available to describe how an "adion" becomes an "ion," what triggers the event, and how frequently it occurs. Clearly, any successful model will have to recognize the quantum mechanical properties of the system, since these determine the electron density about the adion species. Also, any successful treatment must account for the (apparently) labile nature of adions as reflected by their high surface diffusivities and by the wide range of relaxation times that have been observed in impedance studies.

Stochastic Phenomena

Because of the heterogeneous nature of metal surfaces and passive films, corrosion science and electrochemistry often deal with localized phenomena that frequently nucleate in regions of molecular dimensions. Such phenomena, at least during the early stages, reflect the microscopic properties of the surface as embodied in transport, thermodynamic, and reaction kinetic parameters. For example, in the case of pitting attack, it is found that "noise" precedes permanent breakdown, and this has been interpreted as transient rupture of the passive film followed by repassivation (*29-32*). Other studies have shown that the breakdown potential is near normally distributed when a large number of identical specimens is sampled but that the distribution in induction time is not (*29*). These findings have been interpreted in terms of Markovian stochastic models that provide little mechanistic information on the processes involved. Consequently, deterministic models (*32*) are needed for dissolution, film breakdown, etc., that can be married with stochastic descriptions of the processes involved to reflect reality more accurately and to provide a basis for developing quantitative predictive methods for extrapolating corrosion functions into the future.

Stress Corrosion Cracking, Corrosion Fatigue, and Hydrogen Embrittlement

Stress corrosion cracking (SCC), corrosion fatigue (CF), and other localized corrosion phenomena (e.g., pitting attack) account for a significant fraction of corrosion failures in industrial systems. However, the mechanisms (*33*) of crack propagation under SCC and CF conditions are poorly understood, and the potential drop down the crack, the extent of spatial separation of anodic and cathodic partial reactions, whether the crack tip is bare, whether significant hydrogen evolution occurs at the crack tip, the atomistic events that lead to fracture, and the influence of grain boundaries are not known. The resolution of these problems will require the development of new concepts and theories, with input from electrical engineering, metallurgy, electrochemistry, chemistry, physics, solid mechanics, and mathematics. Emphasis should be placed on deriving quantitative models to guide the development of new experimental techniques and to compare with experimental results.

Passivity

In spite of extensive research over the past 150 years, there are at present no adequate models for the chemical, structural, and electronic properties of passive films. Most passive films probably lack the long-range order that is necessary to support well-defined band and crystal structures, and it is likely that significant variations in cation oxidation state occur across the film. The defect structures of passive films need to be investigated to define the types of defects that are present and to determine the distribution of defects within the film. The electronic structure of a passive film is a matter of considerable importance because of the various photochemical and photoelectrochemical processes that occur on oxide-covered surfaces. The coupling that may exist between the electronic and defect structures of passive films is not well understood, but experimental and theoretical developments are now becoming available to address the problem. Also, the transport of defects and other charge carriers through the film and the processes that occur at interfaces are critical issues for the formation and breakdown of the films. The resolution of these problems and others, such as the distribution of space charge in the films, the nature of the metal-film interface, the electric field strength in the film (*34*), the concentration and nature of "dopants" in the film (*35*), the breakdown processes in the film (*36,37*), and the mechanical stability of the film, must come before significant progress is made in the field. Collaborative research efforts seem to be essential for progress.

The existence and role of space charge in passive films continues to be debated by electrochemists, but little progress is being made because of an almost total lack of good experimental data and adequate theory.

This is partly due to the failure of many electrochemists to appreciate the important differences that almost certainly exist between the electronic properties of passive films and classical semiconductors. Redressing this situation will almost certainly involve elements from surface and semiconductor physics, quantum mechanics, charge transfer theory, optics and spectroscopy, mechanics, crystallography, chemistry, and mathematical modeling. The topic is exceedingly complex, but the payoffs are enormous, considering that passivity breakdown is the principal cause of localized corrosion.

Equilibrium Thermodynamics of Aqueous Systems

The thermodynamic behavior of metals in dilute aqueous environments at both ambient and elevated temperatures is now well established, with potential-pH or "Pourbaix" diagrams being available for many metals of technological interest in both complexing and noncomplexing solutions. However, many corrosion processes of present interest (e.g., corrosion of high-level nuclear waste canisters in salt repositories and denting in nuclear steam generators) occur in concentrated solutions, where thermodynamic properties are not available. In extending potential-pH diagrams to concentrated solutions, it will be necessary to employ electrolyte solution theories from chemistry to calculate the variations in solvent activity and ionic activity coefficients with composition in multicomponent systems.

The extension of potential-pH diagrams to alloy systems is also a matter of great interest, because the simple superposition of diagrams for each alloy component is generally inadequate for defining precisely the thermodynamic properties of complex alloy systems. Because the thermodynamic properties of the alloy components and the oxidized phases that form are composition-dependent, it is likely that markedly different potential-pH diagrams will result for different alloy compositions.

Equilibrium Thermodynamics of Molten Salt Solutions

When metals and alloys are exposed to a high-temperature environment that includes molten salts, even in the form of thin films, severe corrosion is likely to occur. Several kinds of salts are known to be aggressive, including alkali chlorates, sulfates, carbonates, and nitrates. A typical example of hot corrosion arises when condensates from the cooled combustion products of fossil fuels, which usually include molten sulfates, form corrosion films on high-temperature alloys used as construction materials. Hot corrosion (*7,8,38-40*) leads to rapid breakdown of protective oxide films and degradation of the underlying material. It is often a design-limiting factor in energy technologies, particularly those based on coal, as well as in propulsion systems. New corrosion control techniques would speed the introduction of improved technologies. There is currently a lack of knowledge both of the mechanisms of attack and of the total chemistry of complex corroding systems. New computational capabilities, more extensive thermodynamic data, and theories (*41,42*) are needed. The development of methods for defining the total chemistry involved in hot corrosion should assist greatly in devising methods for controlling this type of degradation.

NUMERICAL AND SYSTEMS ANALYSIS

Corrosion systems consist of complex interconnected and interrelated components and phenomena. Multiple reactions and processes, distributed laterally across surfaces as well as through interfacial films and changing with time, lead to system behavior that is difficult to analyze. The influences of geometry, thermodynamics, kinetics, transport processes, and the nature of the surface and environment may all be important. In addition, the mechanical state of the degrading solid may affect phenomena such as stress corrosion cracking. The previous section focused on modeling of individual processes or parts of the system, often at a microscopic level, where a detailed description contributes to understanding because of the clear connection between cause and effect. In the present section, emphasis is placed on treating the entire system—i.e., on incorporating individual phenomena in a global analysis of the actual corrosion situation. The analyses that result will aid in the development of test methodologies, expert systems, and prediction strategies and will provide a basis for economic optimization.

One justification for modeling and analysis is that judicious modeling, combined with experiment, is generally less expensive than experimentation alone. Mathematical models (once established) have quantitative predictive capabilities for scale-up and scale-down and, accordingly, can be used in economic optimization. The models have the additional benefit that they provide general insight that may translate into understanding other corrosion phenomena as well.

Computational Methods

The system of equations for modeling corrosion systems may include (a) electrochemical equations, such as Faraday's law and the Nernst-Planck, Laplace, and Poisson equations; (b) hydrodynamic equations, such as the Navier-Stokes and empirical turbulent flow relations; and (c) mechanics equations, such as Hookes' law and fracture mechanics considerations. Electrochemical boundary conditions include potential, solution concentrations, fluxes, and rate expressions. Hydrodynamics and mechanics may also contribute certain boundary conditions.

Rigorous mathematical modeling techniques for electrochemical systems, which have been developed over the past 2 decades by electrochemical engineers, are just beginning to be introduced into the field of corrosion. These correspond to modeling efforts on heterogeneous catalysis and in chemical engineering. Many of the mathematical models become so complex that only numerical solutions by computer are feasible. Nonetheless, analytical, asymptotic limits are useful to supplement the modeling because they give physical insights into the problem as well as simple solutions that may be easily evaluated.

Of all the areas of corrosion science and engineering, cathodic protection has received the most attention for modeling. Together with the closely related process of electrodeposition, it provided early applications for the techniques of the classical mathematical physics of electric fields. Analytic results are available for a large number of geometries (*43*). Inclusion of the effects of interfacial reactions, usually as nonlinear boundary conditions, has led to the use of various approximate and numerical techniques for modeling the behavior of cathodic protection systems (*44*).

Many of the same methods have been adapted to the study of galvanic corrosion, where the coupling of dissimilar metals leads to corrosion of one metal of the couple. Simple rectangular or cyclindrical geometries have been most common for the treatments. Fourier series techniques adapted for numerical analysis on large-scale computational facilities were among the earliest studies in this field (*45* and earlier papers in the series referenced therein). General surface kinetic boundary conditions have been used for the direct numerical analysis of galvanic corrosion with multiple surface sites defined by exposure of a substrate metal through holes and defects in a protective overlayer (*46*). The results have been useful, for example, in developing laboratory tests for determining the porosity of protective metal overlayers. Extension of the modeling to random arrays of corrosion sites will lead to further refinements in laboratory testing of the phenomena, but it will also lead to fundamental advances in describing the interactions of heterogeneities on corroding surfaces.

Mass transfer effects on corrosion have been recently reviewed (*47*). Methods developed for other applications in electrochemical engineering (*48*) have been adapted for corrosion systems but have not yet been widely used. An excellent example of modeling mass transfer effects is in the study of the concentration distributions in crevices (*49*), in fatigue cracks (*50*), and in stress corrosion cracks (*51*). Numerical methods were used in these studies. Perturbation techniques have been used to study similar problems for mass transfer of minor components in various crack geometries (*52*).

These state-of-the-art modeling techniques are not widely used now in corrosion studies, but the situation is changing. Further developments may be anticipated in numerical analysis, as both finite difference and finite element methods become more widely available. Greater knowledge of the available applied mathematics and mathematical physics methods will lead to improved models for corrosion systems. Increased participation by mathematicians in developing models of corrosion phenomena should be encouraged.

Examples of Models

Three examples of model calculations in corrosion science are given here to illustrate the current status and what could be accomplished by efforts in other systems.

Stress Corrosion Cracking

Stress corrosion cracking is an insidious and expensive problem in chemical processing plants, oil and gas wells, nuclear power stations, and other technologies. SCC is a complex phenomenon involving mechanics (stress analysis), metallurgy, and electrochemistry. The critical events at the crack tip occur on an atomic scale in a geometry that is inaccessible to direct in situ observation. Mathematical modeling and testing of model prediction with phenomenological observations provide one of the most promising techniques for developing an understanding of the fundamental processes occurring in a stress corrosion crack. The corrosion of the metal, formation of oxide films, hydrogen ion reduction on the newly generated surface at the crack tip and along the walls, hydrolysis of metal ions in the crack solution, and transport of ions in the solution along the axis of the crack by potential and concentration gradients are all processes that result in concentrations and potentials in the crack tip region that may be very different from those in the bulk solution outside of the crack.

Some first-generation models have been published for a few SCC systems (*51,53,54*). Turnbull (*49*) modeled the behavior of oxygen in a stress corrosion crack and found that it reacted in the outer part of the crack. Modeling efforts have advanced well beyond these first-generation contributions. Several groups have coupled localized crack electrochemistry concepts with continuum and micromechanical fracture processes to derive expressions for environmental cracking. These contributions have recently been summarized (*55*). Continuing this type of work is essential since (a) mechanistic research is incomplete, and more sophisticated modeling and crack process measurements are required, and (b) such modeling provides a crucial element in the formulation of methods for predicting and monitoring complex system behavior. The modeling approach, uniquely designed for each metal and environment, offers the opportunity of quantitatively predicting the electrochemistry of SCC at a fundamental level. In the future, models combining electrochemistry with fracture mechanics not only will allow a more complete understanding of SCC but also will provide predictive capability for specific metal-environment-stress situations. Success with one system will lend encouragement to the description of other systems and will lead to general understanding for control or avoidance of costly stress corrosion cracking problems.

Electrokinetic Corrosion

A recent technological corrosion problem solved by a multidisciplinary basic research effort was that of "valve erosion" in commercial jet airplane hydraulic systems (*56*). The problem was one of wear of the steel metering edges in the hydraulic control valves that operate the flight control surfaces and wheel brakes. A multidisciplinary team composed of a fluid dynamicist, a plasma physicist, and an electrochemical engineer discovered that the wear was corrosive in nature and was driven by the generation of electrokinetic streaming currents. Theory and modeling suggested several new approaches to solve the problem, and indeed, development of quantitative theory was essential in finding possible solutions. One was to increase the fluid conductivity by adding a few hundred parts per million of conducting salts to the fluid. The increased conductivity compressed the diffuse electrical double layer and decreased the streaming currents, virtually eliminating corrosion.

Thermodynamic Calculations in Complex Systems

Advanced computational techniques and computer aids have made possible the calculation and representation of the thermodynamics and equilibrium properties of complex multicomponent-multiphase systems (*41,42*). In addition, it is possible to incorporate certain known kinetic factors into the calculations to determine important aspects of the nonequilibrium chemistry of corrosion. When coupled with coordinated experimental studies, these techniques will permit the total chemistry of many types of complex corrosion phenomena to be elucidated. For example, at high temperatures, calculations could be performed to define the complex multicomponent protective oxide solid solutions (e.g., spinels) formed in the corrosion of a complex alloy. Similarly, calculations could be performed on the total system chemistry for gaseous and molten phase corrosion of an alloy by the complex effluent from the combustion of coal. Some of the mathematical techniques are available to handle such complex systems analysis, but more work is essential for significant progress. Two of the limiting factors in using advanced calculational techniques are the lack of thermodynamic data for a number of materials and the lack of adequate understanding of kinetic factors. The development and use of advanced mathematical techniques coupled with an adequate thermodynamic and kinetic data base will provide guidance for the control of corrosion in many technologically important systems.

Research Opportunities

It is clear that a major limitation in present corrosion science and engineering is the lack of well-developed techniques for analyzing complex corrosion systems as a whole. This limitation is both conceptual and numerical; few corrosion problems are analyzed by considering all of the various phenomena that may affect the system of interest, and the corrosion field has rarely used the powerful computational techniques that have been developed in other areas of science and technology. As a simple example, pitting corrosion is usually discussed in terms of passivity breakdown and the anodic reactions that lead to pit propagation, but seldom are the kinetics of the cathodic reaction taken into account or the potential and current distributions external to the pit considered. With respect to the second point, highly efficient and flexible mathematical techniques have been developed for solving multiple coupled nonlinear equations that describe the chemistry and physics of complex systems. These have not yet been applied in corrosion science but offer the opportunity for significant advances in the near term.

Efforts focused on the mathematical modeling of several corrosion systems would provide both application-specific benefits and general advancement of the field through improved understanding of corrosion processes. Mathematical modeling of corrosion systems does have two limitations: It must be closely coupled with the experiment or it will become irrelevant, and it must have at hand relevant physical and chemical property data, which are often not available, particularly for concentrated solutions and extreme conditions. The following systems should be considered:

- Corrosion Processes—Although some preliminary models have been formulated, pitting, crevice corrosion, and stress corrosion cracking are only partially understood. For each of these complex corrosion systems, modeling provides an approach to the determination of critical factors such as breakdown voltage, induction time, and the distributions in these quantities; these factors can now only be inferred from experiment.

- Protection Strategies—Most cathodic protection systems are still designed by rules of thumb. Modeling clearly offers the opportunity for optimization of cost and performance in this area. Protection of increasingly ubiquitous and sensitive solid-state electronic devices requires better quantitative understanding. The very small scale and the need for evaluations of long-term reliability make electronic devices ideal subjects for modeling studies.

EXPERIMENTAL TECHNIQUES

Progress in corrosion science and engineering would be considerably enhanced by more satisfactory in situ techniques capable of determining film and surface structure, composition, and physical properties and capable of following dynamic corrosion processes in real time. It is clear that advances in this area would support the development of theories and models capable of predicting corrosion behavior in unknown systems and providing guides to the design of critical experiments. Three recent reviews have described the state of the art of experimental techniques that can be used to study electrode processes of importance to corrosion (*57-59*). The most recent review (*59*) suggested that some progress has been made in bringing electrochemistry to the point where solid-vacuum studies were 15 years ago. Since the electrochemical interface is, however, considerably more complex than the solid-vacuum interface, "the molecularly sensitive techniques available for its characterization are considerably more limited" (*60*). In addition, two workshops have brought these developments up to date (*61,62*). These workshops have revealed that an array of new and modified older techniques has come on the scene in recent years, promising in situ information that will advance significantly the understanding of corrosion processes. For corrosion in particular, more so than for some other areas of electrochemistry, the most useful techniques concentrate on the films, usually three-dimensional films, that are crucial elements in controlling corrosion processes. A useful summary of some of these techniques is given in Table 1.

These new experimental techniques provide tools that can characterize the structure, measure electronic, optical, electrical, and mechanical properties, and describe the corrosion processes occurring at the metal-film-electrolyte interface. In addition, an important advance that is more an approach rather than a technique is the increasing use of well-defined single crystal surfaces (*63*). The combination of powerful new experimental techniques used in studies carried out on well-defined surfaces with advanced modeling approaches and new concepts and theories of corrosion augurs well for the future. The new experimental techniques that will play a role in advancing corrosion science provide insights into the following major aspects of corrosion phenomena: structure, composition and valence state, physical properties, and processes.

Research Opportunities

Corrosion science, like all of the physical and chemical sciences, is still basically an observational activity in which concept and theory provide the intellectual framework within which experimental data are interpreted and predictions made. The theories and predictions are

TABLE 1 Summary of Nonelectrochemical Techniques Useful in Studying Passivity of Metals

Technique	Major Advantages	Major Disadvantages	Information Obtained
Ellipsometry	In situ studies possible; applicable to kinetics of film repair	Must have planar, highly reflective surface	Film thickness; refractive index of film
Electron Diffraction	Structural information obtainable	High vacuum must be used	Crystallographic information
Electron Microscopy	High magnification possible	Depends on system	Morphological information on a microscale
Mössbauer Spectroscopy	In situ studies possible	Limited to few metals; interpretation of spectra difficult	Film composition; valence state; magnetic properties; crystal size
Auger Electron Spectroscopy	Can analyze for all elements except H and He	Must use high vacuum; possible radiation damage to sample	Elemental composition; depth profiling
X-Ray Photoelectron Spectroscopy	Can analyze for all elements except H and He; information on binding energies	Must use high vacuum	Elemental composition; depth profiling
Low Energy Ion Scattering Spectroscopy	Can analyze for all elements except H and He; information on binding energies	Must use high vacuum; insensitive to elements of low at. no.; surface sputters as analysis is carried out	Elemental composition; depth profiling
Isotope Studies	Advantages, disadvantages, and information generated dependent upon system		
Soft X-Ray Spectroscopy	Information on binding energies	Interpretation of data difficult; must use high vacuum	Valence state and binding energies
Modulation Reflection Spectroscopy	In situ studies	Limited information obtained; interpretation difficult	Band gap for passive film
Semiconductor Properties	Advantages, disadvantages and information generated dependent on system		
Neutron Activation Analysis	Sensitive technique for some elements	Limited usefulness; requires stripping of film from substrate	Elemental composition

SOURCE: H. Leidheiser, Jr. (64). Used with permission of the publisher, The Electrochemical Society, Inc.

frequently limited by the quantity and quality of the experimental data bases, which in turn are determined by the quality of the experimental techniques employed. The principal problem at present is to develop techniques that are capable of probing corrosion systems at atomic and molecular dimensions and on bond vibrational time scales. Many techniques having these characteristics have been developed, but few have been developed to the extent that they can be applied in situ in the study of corrosion processes. Emphasis in the future should therefore be in the adaptation of these techniques for use in condensed media. With successful developments in this area, it is reasonable to expect the following accomplishments:

- Development of techniques and instruments that are capable of probing interfaces on dimensional scales that are relevant to the phenomena of interest

- Development of techniques for probing interfaces in condensed media

- Improvements in the quality of the data bases that are used in corrosion science

- More precise and useful theories that have been critically tested against experimental data of high quality

The discussion that follows is broken into two general categories relating either to research opportunities of a general and fundamental nature or to research opportunities that are specifically appropriate for localized corrosion.

Fundamental Experimental Techniques

Structure. One critical factor in determining corrosion behavior is the nature of the film that exists on every metal surface that has technological value. Reveze and Kruger (*65*) have emphasized the important role that the structure of these films plays in controlling corrosion. For example, they suggest that films with vitreous structures residing on metal or semiconductor surfaces provide more corrosion resistance than films with crystalline structures. The new in situ x-ray absorption technique EXAFS (extended x-ray absorption fine structure) has been used to show how the structure of a passive film becomes more vitreous with the addition of alloying elements to the metal on which the film is formed (*66*). Thus, knowledge of how alloying affects passive film structure can be used in the future to design alloys that are more corrosion-resistant. However, the fundamental causes of structural changes are not understood, so current predictive capabilities are severely limited.

Because the structures of films may change considerably upon removal from the environment in which they are formed, in situ techniques are particularly desirable. The information required from these studies includes the extent of long-range order, the existence and role of water, the nature of bonding between different phases within the film, and the identification of metal-metal and metal-ligand bond type within the film.

Many of the advanced experimental techniques capable of in situ characterization of the structure of films, especially the passive layers that control corrosion processes, are optical. The principal methods are the vibrational-spectroscopic techniques (surface-enhanced Raman, SER); Fourier transform infrared (FTIR), photothermal, and internal and external reflection spectroscopies; ultraviolet-visible reflectance; and fluorescence spectroscopy. Another optical tool that can provide insights into structure at the molecular level is spectroscopic ellipsometry. The most pressing need for the future is to improve the lateral resolution of these techniques so that they can be used to probe structural inhomogeneities with dimensions less than 1 μm x 1 μm. This necessarily will require the development of more powerful light sources and more sensitive detectors. Furthermore, the large amounts of data that will be generated in spectroscopic scans across real metal surfaces will require the use of significantly enlarged data storage and processing systems.

Of more recent vintage are the structural tools that use x-rays or electrons. Those that are capable of making in situ measurements are EXAFS, which can determine bond distances in passive films using synchrotron radiation, x-ray scattering and standing-wave techniques, and electron tunneling microscopy, which can provide micrographs of such resolution that the atoms in a crystal structure can be seen (*67*). New ex situ techniques using x-rays or electrons include EXAFS (using hard and soft x-rays), which can provide bond distance information for low-atomic-number elements such as oxygen, and low- and high-energy electron diffraction. Recently it has been reported that photoelectrochemical techniques can distinguish between vitreous and crystalline passive films (*68*). It is still uncertain whether the new technique of scanning electron tunneling microscopy (SETM) can provide useful in situ structural information because the results obtained contain an unknown mixture of structural, compositional, and electronic structural data. It will be necessary to focus attention on simple systems where these contributions can be separated to assess the usefulness of the SETM technique.

Composition and Valence State. As with structure, the composition and valence state of the elements that exist in the films on metal surfaces play important roles in determining the properties of these films. Unlike film structure, the structure of the substrate (single crystal or heterogeneous) on which the films are formed is not important. Substrate composition and the variation of this composition with microstructure are, however, of great importance. This arises because composition affects the structure of a film (for example, high chromium content promotes vitreous films for ferrous alloys), and compositional variations of an alloy with microstructure can lead to film compositional and structural heterogeneity—a condition that provides sites where localized corrosion can be initiated. Hence, techniques, such as scanning Auger electron spectroscopy, that can determine composition and valence state with good spatial resolution can provide insights into localized corrosion processes.

Almost all of the techniques that can provide composition and valence state information about the metal-film-electrolyte interface are carried out in ultrahigh vacuum and are therefore of necessity ex situ techniques. One notable exception is Mössbauer spectroscopy, which has been used in in situ studies of passive films (*69*). The ex situ techniques that have been applied in corrosion studies in recent years include Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), low-energy ion-scattering spectroscopy (ISS), secondary ion mass spectroscopy (SIMS), and soft x-ray spectroscopy. These techniques have proved to be among the most powerful available for the study of films, and their continued development is to be encouraged. It is, however, equally important to establish firm correlations between the results of ex situ measurements and in situ compositions, particularly for films generated in condensed media.

Physical Properties. For corrosion studies a major concern is the physical (optical, electronic, electrical, magnetic, and mechanical) properties of films (such as passive films) and adsorbed layers (of inhibitors, etc.). Optical properties are provided by the spectroscopic techniques described earlier in the section on structure. The electronic properties of main concern are those associated with passive layers that are semiconductors or insulators. Usually, the structural nature of the substrate has little influence on the measured physical properties of these films because the determination gives an average over the whole film in all three dimensions. Great improvements in the understanding of localized corrosion processes would ensue, however, if techniques existed that could determine physical properties at discrete sites. The determination of the physical properties of films, on the average or at discrete sites, addresses the critical issue of how electrons, ions, and defects move through films; this is of importance in developing mechanisms and models of passive film formation, breakdown, and repassivation. The response of a film to tensile stress—information obtained by measuring the mechanical properties of the film—is greatly needed in the development of more effective models of stress corrosion processes.

One group of in situ techniques being applied is photoelectrochemical in nature. Among these are photocorrosion techniques, transient photocurrent measurements, and surface plasmon excitation studies (*70*). Other in situ techniques that measure electronic properties are some of the optical techniques described earlier—for example, modulation reflection spectroscopy, which provides band gaps of passive films (*71*), and near-edge x-ray absorption spectroscopy (XANES), which is carried out during EXAFS measurements (*72*). The semiconductor properties of passive layers have been determined by electrochemical techniques that measure electron transfer reactions and resonance tunneling on the surfaces of these layers (*73,74*). An exciting prospect exists that combined photoelectrochemical and AC impedance spectroscopies can be used to explore coupling between the electronic and defect structures of passive films, as has been shown by the photo-inhibition of passivity breakdown (*75*). Quantitative definition of this effect is essential if suitable models are to be developed to describe the electronic and structural nature of passive films.

Electrical properties, such as resistance and capacitance, can be determined in situ using thin metallic film electrodes (*64*) and the electrochemical technique of AC impedance spectroscopy (*76*). Only one technique—Mössbauer spectroscopy—appears capable of providing in situ magnetic properties (see Table 1). Finally, the mechanical properties of passive layers, which are important in stress corrosion mechanisms, have been determined by a straining electrode technique (*77*) that gives the ductility of the passive film.

Processes. The experimental techniques discussed thus far provide a base of information that is needed to interpret the results obtained from the techniques that examine corrosion processes. The techniques that examine the corrosion process itself as it is occurring are, of necessity, all in situ. Thus, these techniques determine the kinetics of the many forms of corrosion and the processes that affect them, such as passivation, breakdown of passivation, and repassivation. These approaches include both electrochemical and nonelectrochemical techniques.

Most of the electrochemical techniques involved in studying corrosion processes have been described in a review on electrochemical techniques for the study of passivity (*76*). The electrochemical techniques used to study corrosion processes, especially kinetics and localized corrosion, include impedance spectroscopy, DC transient techniques, potential scanning and mapping (*78*), electrochemical noise (*79*), and electrochemical measurements of hydrogen permeation (*80*), as well as the many more usual polarization techniques (*76*). Two recent texts have discussed general test techniques for corrosion engineering (*81,82*).

In situ nonelectrochemical techniques that can be used to study corrosion processes include ellipsometry to study adsorption, film formation, dissolution, breakdown and repassivation (*83*), pitting (*84*), crevice corrosion (*83*), and corrosion processes under organic coatings (*85*); electron microscopy of environmental effects in stress corrosion and hydrogen embrittlement (*86*); laser interferometry and holography; and optical microscopy.

Experimental Techniques for Localized Corrosion

Localized corrosion is the principal cause of technologically important corrosion failures such as stress corrosion cracking and pitting. Therefore, research opportunities in this area are described separately here.

Several techniques have been developed either to provide a reliable and critical method to determine susceptibility to localized corrosion or to reveal the mechanism by which the attack occurs. These include

- pitting and crevice exposure tests (*87,88*)
- environmental fracture techniques (*89-92*)
- electrochemical cyclic potentiodynamic (*93*), potentiostatic (*93,94*), and galvanostatic techniques
- pit propagation rate (*95*)
- optical-electrochemical techniques (*96*)
- electrochemical noise (*97,98*)
- localized corrosion environments (*99*)
- statistical data analysis for initiation and propagation of localized attack (*100*)

From the understanding of localized corrosion processes, four significant aspects can be identified that appear to be of the utmost importance in suggesting the basis for research that will lead to more reliable test methods.

The Existence of an Induction Period. The existence of an induction period, whatever the processes are that control it, is a measure of the time for pitting or crevice corrosion to initiate. Thus, a test that can measure the induction period will also measure the time for initiation to take place. Although such tests exist (one simply holds a specimen above E_p, the pitting potential, by means of a potentiostat and measures the time required to observe a rapid increase in anodic current), induction times can be too long (greater than a year) to be measured in a reasonable test period. There is no basis available at the present time to predict or measure long induction times for initiation of localized corrosion. This prevents development of accelerated tests to determine the time required for initiation of localized attack. Once pitting or crevice corrosion is initiated, however, test methods (*95*) can give a value for the rate of propagation. This value can then be used to estimate the time required for penetration of the wall of a vessel.

The Existence of Critical Potentials. The major mechanistic and testing problem associated with critical potentials is the confused state of the literature concerning "critical" potential values and procedures for their determination. In defining these values, concepts of initiation and propagation have often been intertwined. Therefore, a better understanding of the localized corrosion process is needed to define more clearly the important critical potentials and how they may be obtained experimentally. With this in mind, it should be possible to develop accelerated test methods that reflect real-time values for the initiation time and propagation rates for the localized corrosion of alloys in a specific environment.

The Role of Repassivation. Some of the definitions of a critical potential make it the potential below which repassivation takes place at a high rate. On the other hand, some theoretical models reserve an important role for repassivation in breakdown (i.e., initiation) processes. Propagation is supposed to proceed when repassivation can no longer choke off initiation. Some of the test methods described earlier, therefore, evaluate the possibility for breakdown of passivity and propagation of localized corrosion of a given alloy in a relevant environment at a given potential by measuring the rate of repassivation. The validity of the assumption must be demonstrated in each system.

The Role of the Local Environment. Since most pitting and crevice corrosion mechanisms involve a change in the local environment in a pit or crevice, this environment should be the most relevant test environment. The first task in establishing the validity of the local environment as a test medium, actually an accelerated test medium, is to characterize the local environments that develop in pits and/or crevices for a given alloy in a given ambient environment. Once the composition of these environments is known and the validity of their use as test media is established, such environments would be the most relevant ones to use to measure critical potentials, pit or crevice propagation rates, or repassivation rates.

MONITORING OF CORROSION

With the advent of more complex technological systems (e.g., nuclear reactors, refineries, fossil fuel power plants, and chemical processes), corrosion has become a critical issue in maintaining system availability and viable economics. Indeed, experience in the nuclear industry over the past 2 decades has shown that corrosion is a leading cause of plant outage or unavailability, costing on the order of $500,000 per day for power replacement for a typical commercial 800-MW(e) plant. Clearly, an enormous incentive exists to develop monitoring techniques for detecting various forms of corrosion and serving notice that remedial measures must be taken. New and more effective corrosion monitors are also required for laboratory studies, so that the kinetics of various forms of corrosion can be accurately defined. This is particularly the case for corrosion phenomena that occur under conditions of extreme temperature and pressure, where direct visual examination of a corroding surface frequently is not possible.

In assessing the need for new monitoring techniques, it is advantageous to divide corrosion processes into general attack and localized attack. In the first case, the spatial distribution of attack is not an issue, whereas in the second, attack is normally confined to very small areas on the surface. Although the weight loss in localized corrosion may be very small, the rapid penetration rates commonly associated with localized attack can lead to unexpected failures in short times. Indeed, in the case of "corrosion-resistant" alloys, such as stainless steels and high-nickel alloys (e.g., Alloy 600), localized attack is the predominant cause of failure.

The principal goals of monitoring are to detect the onset of corrosion, to determine how far the damage has proceeded, and to predict the probability of failure at some future time. Given sufficient resources, it is likely that significant advances can be made in this area over the short term (10 to 15 years) and that sophisticated monitoring systems will result over the much longer term.

Current Practices

Current electrochemical monitoring techniques are based largely on the "linear polarization" procedure that was originally described by Stern and Geary (*101*) and later developed by Mansfeld (*102*). The basis of this method is the determination of the polarization resistance (R_p) of the interface by perturbing either the current or the potential in small steps about the open circuit state. The corrosion current is then calculated, usually under the assumption that both the anodic and cathodic rates depend exponentially on potential. The method has the advantage of yielding instantaneous corrosion rates and is readily adapted for use in situ in aggressive environments. However, as noted by Syrett and Macdonald (*103*) and others (*102*), it has a number of shortcomings:

- Because the polarization resistance frequently changes rapidly with time, it is necessary to monitor R_p at short times if accurate corrosion rates or weight losses are to be calculated.

- It is essential that the "polarization resistance" be measured at sufficiently low voltage sweep rates (small-amplitude cyclic voltametry), low frequencies (AC impedance spectroscopy), or long enough times after imposition of a perturbation (current and voltage step techniques) that the interfacial impedance is nonreactive. However, the impedance of corroding interfaces normally becomes more reactive with time, so that the minimum voltage sweep rate and AC frequency that must be used for sampling the interface must be reduced as sampling proceeds. This problem has been discussed at length by a number of authors (*101,104,105*); if suitable precautions are taken, the linear polarization technique will yield reliable instantaneous corrosion rates in most cases (*102*).

■ Because linear polarization techniques generally sample the interfacial impedance only at a single frequency or only over a very narrow frequency band at which the system is nonreactive, very little mechanistic information is obtained. However, by using multifrequency perturbations (*106-108*) or noise analysis (*109,110*) or by examining nonlinear effects (*111,112*), it should be possible to obtain the desired mechanistic information without significantly complicating the measurement as far as the experimenter is concerned.

For localized corrosion (pitting, stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, crevice corrosion, and intergranular attack), existing monitoring techniques to measure electrochemical conditions within the occluded regions are rudimentary in nature, and few provide instantaneous measures of the corrosion damage as it proceeds. However, sophisticated sensors based on direct or alternating current or potential have been demonstrated to accurately monitor slow crack growth in laboratory specimens exposed to a wide variety of very aggressive environments. Recent work has successfully applied these techniques to monitor SCC and corrosion fatigue crack growth in both surveillance specimens and in prototype component configurations exposed to nuclear and offshore environments (*89-92*). At the same time, pitting corrosion, crevice attack, and intergranular corrosion are almost always detected by post-test examination of suitably configured specimens. Future efforts to develop the crack monitors for a wider variety of applications and to develop in situ techniques for other localized corrosion tests would be of great value because of the damage caused by these forms of attack.

Research Opportunities

Significant opportunities exist for applying electrochemical and ancillary techniques for in situ monitoring of corrosion in both ambient- and elevated-temperature aqueous systems and in molten salt electrolytes. The principal thrust should be in exploring new techniques for sampling the properties of a corroding interface, with the objective of determining not only the corrosion rate but also the mechanism of attack. Significant improvements can be made in existing monitoring methods, and new techniques might be devised by transferring technology from other areas of science and engineering, particularly from electrical engineering, where sophisticated methods have been developed for determining the properties of complex electrical circuits. Also, a number of spectroscopic techniques might be employed to provide information on surface structure and composition; however, it is stressed that these techniques must be applicable in situ if they are to be accepted for monitoring purposes.

A number of the more important techniques for monitoring specific forms of corrosion, together with perceived advantages and disadvantages, are outlined here.

AC Impedance Spectroscopy (ACIS)

In AC impedance spectroscopy (*104,105*), the corroding interface is perturbed using a small-amplitude sinusoidal voltage or current, and the interfacial impedance $Z(\omega)$ is measured over an effectively infinite frequency range. The polarization resistance is then determined from the impedances at infinite and zero frequencies, and the desired mechanistic information may be gleaned from the frequency dependence of $Z(\omega)$. The major disadvantage of ACIS is that the data acquisition time may be excessively long if data are required at very low frequencies. However, data analysis techniques are well developed, and ACIS can be applied to highly resistive systems (e.g., pure water). The principal advances required in ACIS are to develop more efficient methods for extracting mechanistic and kinetic information and to reduce the cost of the equipment.

Structured Noise Analysis (SNA)

SNA is identical in concept to ACIS except that the system is perturbed by a composite signal synthesized from a large number of sine waves having the desired frequencies, amplitudes, and phases (*106-110*). The interfacial impedance is calculated using an integral transform (Fourier or Laplace) and is then analyzed to extract the polarization resistance and mechanistic information in a manner that is identical to that for ACIS. The major advantage of SNA is that the data acquisition time is determined only by the lowest frequency component rather than by the sum of reciprocal frequencies, as for ACIS. The technique is very flexible, in that a wide variety of perturbing signals may be synthesized, including "white," "pink," "semi-random," and highly "structured" noise, to suit the experimenter. Although the technique has only been used in a few instances, it is apparent that it is completely equivalent to other techniques that emphasize a Fourier analysis approach to the problem. With the advent of 32-bit and 64-bit digitizers and microprocessors, this technique will become more widely used in the future.

Self-Generated Noise Analysis (SGNA)

All corrosion processes generate electrical noise due to a variety of microscopic phenomena, and a number of attempts (*109,110*) have been made to use this noise to monitor the rate of corrosion. The principal advantage is that no perturbation need be applied to the system, so that the instrumentation is relatively simple (at least in principle). Also, some evidence exists that the technique might be capable of distinguishing between general corrosion and localized attack. The major disadvantage is that data analysis techniques are very poorly developed and the potential of the method is almost completely unexplored.

Harmonic Analysis

The use of large-amplitude perturbation techniques in the monitoring of corrosion processes has been explored and shows considerable promise because of the large amount of information that can be generated (*111,112*). Although data analysis is somewhat more difficult than for ACIS, it is comparable to that for SNA and SGNA. Previous applications of this technique have been largely restricted to "Faradaic rectification," but more recent studies indicate that the method might be applicable to cathodically protected systems.

Kramers-Kronig Analysis

ACIS and SNA both seek to determine the complex impedance of a corroding interface by measuring independently the in-phase and quadrature components of the response. The complex impedance is then generated directly by hardware (e.g., by frequency-response analyzers or phase-sensitive detectors) or by software. In principle, the same data can be obtained by measuring the magnitude of the impedance over an effectively infinite frequency bandwidth and then computing the phase angle using the Kramers-Kronig transforms (*113*) This technique would seem to offer the advantages of simple and low-cost hardware and relatively simple software for carrying out the K-K transform. From then on, data analysis would be similar to that for ACIS and SNA. This monitoring technique has not been explored.

Controlled Hydrodynamic Techniques (CHTs)

CHTs (e.g., rotating disks, cylinders, and vibrating wires) have been developed for corrosion monitoring and testing at ambient temperature, but few have been designed to operate at the elevated temperatures and pressures of interest in many industrial and energy systems (*114*). CHTs with calibrated hydrodynamic and mass transport characteristics need to be developed so that quantitative data may be obtained for corrosion processes under realistic environmental conditions. These techniques must also incorporate electrochemical control for many of the monitoring methods discussed here to be applied.

Scanning Microelectrochemical Probe (SMEP)

SMEPs have been used extensively over the past few years to investigate the birth, growth, and death of corrosion pits at ambient temperature, and this work has recently been extended to environments at elevated temperatures (*115*). The use of composite reference and counter microelectrodes raises the possibility of applying many of the techniques outlined here to the study of microscopic features on the surface; at the same time, including computer control ensures accurate mapping of the evolution of localized corrosion phenomena with time, rendering the technique highly suitable for studying the dynamics of localized attack. Devices of this type have been developed for use in the laboratory, but no applications to corrosion monitoring in the field are known.

Stochastic Analysis

Over the past few years it has become evident that many localized corrosion phenomena (e.g., nucleation of pits and cracks) are stochastic in nature; that is, they can be described in terms of statistical distribution functions. Techniques need to be developed for monitoring arrays of specimens simultaneously (*29,30*) so enough data may be generated under identical conditions that statistically significant distribution functions can be obtained. At first sight this task appears to be tedious, but by using microcomputers, large amounts of data can be acquired and analyzed with minimal intervention on the part of the experimenter.

Acoustic Emission and Ultrasonic Techniques

Acoustic emission has been explored as a means of detecting crack propagation, particularly when crack growth occurs discontinuously—e.g., as in hydrogen embrittlement (*33*). The technique has been adapted to the investigation of large structures and pipelines (*116,117*) to detect large flaws. Small flaws and propagating cracks are still below the detection limits of routine instrumentation, but new developments would bring the technique into more common use. This will require detailed analysis of the amplitude and frequency of the emissions and the development of algorithms for relating these data to crack velocity.

Fracture Mechanics Testing

A major effort is required to develop SCC and/or CF crack propagation monitoring techniques that can be used in high-temperature, high-pressure environments, particularly in the field. Monitoring of load relaxation in fracture mechanics specimens loaded under constant displacement conditions has proved to be effective in the laboratory (*118*) and considerable progress has been made over the past 15 years. The need is to develop an integrated fracture mechanics measurement and life prediction modeling method for environmental fracture applications. The components exist to achieve this goal (*55,119,120*), but the synthesis remains to be carried out.

Hydrogen Analyzers

The analysis of hydrogen evolved on the "wet" side of a corroding interface would seem to be a reliable technique for detecting material degradation in closed systems (e.g., nuclear steam generators). The hydrogen probe developed by Yamakawa et al. (*121*) may find use in such application. However, there are currently no simple, inexpensive, and reliable hydrogen monitors that can measure dissolved hydrogen in aqueous environments at levels less than one part per billion. Similarly, there is a need to develop reliable monitors for hydrogen in metals because of the need to detect conditions that might lead to hydrogen embrittlement (*33,121*).

Spectroscopic Monitors

Further development of in situ spectroscopic techniques for use in conjunction with electrochemical corrosion monitors is required to generate information on the structure and composition of surface corrosion product films. The most promising technique seems to be laser Raman scattering using light pipes to transmit the incident and scattered light to and from the surface. However, visible-ultraviolet techniques may also be useful for detecting dissolved species and colloidal products being released from a surface either by monitoring absorption or by examining light scattering.

Specific Ion and Compound Sensors

Many corrosion problems can be attributed to the build-up of one or more aggressive species in the environment. For example, the formation of "yellow water" in stainless steel tanks and the nucleation of pits on this same material frequently arise from the ingress of oxygen and chloride ions, respectively. In many instances, the cause is even less direct; the stress corrosion cracking of Type 304 stainless steel in boiling water nuclear reactors is caused by the radiolytic generation of oxidizing species by irradiation of water in the reactor core (*122*). The detection and control of these corrosive species is therefore a matter of great and urgent importance. However, progress in devising suitable detectors has been slow; for example, pH electrodes (*123-125*) that can operate under reactor conditions (285°C) have been developed only over the past 3 years, and none have yet been installed in an operating plant.

The development of sensors based on electronic materials (e.g., ISFETS) to detect specific components of a corrosive environment represents a major breakthrough in the sensor field. However, other materials, such as permselective polymers, glass, and inorganic membranes, also offer considerable promise for the development of sensors. The challenge at present is to devise cost-effective sensors that act reproducibly under the harsh conditions that frequently exist in industrial environments. An example of such a sensor is that used to detect changes in coolant chemistry in automotive systems (*126*).

General Considerations

Most corrosion failures, whether they are gradual or catastrophic, are preceded by changes in the system that render the environment more aggressive. Furthermore, all failure processes telegraph the pending event. Accordingly, either the conditions that are conducive to attack or the corrosion reaction itself, in principle, can be detected if suitable sensors are available. The savings to industry and the public at large would be in the range of billions of dollars if the onset of failure processes could be detected prior to their culmination in a catastrophic event. Areas of particular interest for research on and development of sensors and monitoring techniques include the following:

- Sensors to detect and measure aggressive species (e.g., Cl^-, H^+, $(S_2O_3)^{--}$, H_2) in high-temperature aqueous systems of the type that exist in deep geoenergy reservoirs, in nuclear power plants, and in supercritical fossil power generating facilities

- Sensors to measure the properties of surface salt films at combustion temperatures to minimize or at least control the "hot corrosion" of gas turbine components

- Sensors to detect the onset of localized corrosion phenomena (pitting, crevice corrosion, stress corrosion cracking), particularly in inaccessible locations. For example, monitors that could detect the onset of fracture of steam generator tubes in pressurized water nuclear reactors or that could signal the nucleation of pitting attack of steels in prestressed concrete would find extensive use in the power generation and infrastructure sectors of the economy.

The list of techniques and needs given here is by no means exhaustive, but those selected highlight some of the more pressing needs in corrosion monitoring. A common feature of all of the techniques and needs is that they require considerable input from technologies outside of the arena of electrochemistry, and yet they still are "electrochemical" in nature. Clearly, the development of suitable monitors must be an interdisciplinary effort.

LIFE PREDICTION AND ACCELERATED TESTING

Perhaps the most difficult task of corrosion scientists and engineers is the prediction of the useful lifetimes of engineering materials. A critical example of this problem is the prediction of the time that will be required to breach nuclear waste containers, which are expected to be buried, with no possibility of retrieval, for periods as long as 1000 years. A large number of the engineering alloys that have been developed for corrosion resistance have an experience history of only 50 to 100 years, and many have been developed within the past 25 years. Furthermore, tests for predicting lifetimes must, to provide timely and useful results, be conducted in periods ranging from hours (e.g., polarization tests) to a few years (e.g., long-term atmospheric exposure tests). In many cases life prediction is based on empirical evaluation of in-service failures, but there is often inadequate documentation of the relevant material and environmental variables, and the causes and remedies are seldom widely disseminated. Accordingly, this section describes some of the immediate and future needs for the development of accelerated testing and life prediction methods. A general requirement for all accelerated testing is the establishment of test protocols that ensure that the tests produce data of sufficient quality and quantity to make reliable, statistically sound predictions. This can only be accomplished if there exist verifiable life prediction models based on fundamental mechanisms that relate the accelerated test results to long-term component performance.

Research Opportunities

General Corrosion

Models for describing general or uniform corrosion rates as functions of time are often empirical and are commonly based on simple exposure tests, followed by weight loss or weight gain analyses and the fitting of curves to the data. Although many of these approaches are valid for interpolation, few are acceptable for extrapolation, since corrosion rates typically vary with time and, for example, are often very low after an initial transition period. In the absence of verified life prediction models based on fundamental mechanisms, there is a need for the compilation of very-long-term exposure and performance data for inclusion in data bases that are accessible to the entire engineering community, replacing the classical "handbooks" of today. These data must be collected, assessed, and stored in some central facility in much the same way that thermochemical data are collected and disseminated by organizations such as the National Bureau of Standards and the International Union of Pure and Applied Chemistry. They would, of course, find immediate use in the practice of corrosion engineering, but they would also serve as a basis for the development and testing of mechanistically based models for life prediction.

At a somewhat more fundamental level, electrochemical test methods for determining instantaneous corrosion rates, such as linear polarization resistance or quantitative coulometry, can be used to determine the parameters in life prediction models. These methods need to be evaluated over long periods of exposure in many environments to assess their usefulness.

Sound life prediction models are essential in making extrapolations in time. They are no less important in interpreting the effects of accelerating factors, such as increased temperature or some other controllable parameter, and in establishing whether or not accelerating conditions have altered the failure process mechanisms.

The variety and complexity of the effects caused by alloying and alloy processing greatly complicate the development of life prediction models for these materials, where, for example, relatively small changes in composition can have major effects on performance. It may well be necessary to couple empirical methods with a fundamental mechanistic approach in dealing with the behavior of alloys, and this is certainly an area where a comprehensive data base of the type previously discussed would be of value.

A final factor influencing the life prediction in general corrosion is the effect of galvanic coupling on the corrosion rate. At present, the few data that are available for specific environments (e.g., the galvanic series in sea water) give only qualitative assessments of the behavior of the active component of a corrosion couple. A data base covering the corrosion rates associated with specific couples in a wide variety of specific environments is badly needed. It would support the development of life prediction models for such systems.

Localized Corrosion

As insidious as general corrosion can be, localized corrosion (pitting, crevice corrosion, de-alloying, etc.) is perhaps the most difficult area of corrosion to deal with in terms of life prediction. Few models exist that correlate alloy or environmental chemistries with pit or crevice growth rates, and there are virtually none available that can accurately predict incubation times. The subject of localized corrosion is still not well understood with relation to environment specificity; to ionic, molecular, or atomic interactions with passive films; and to potential fields. The perhaps tedious, but certainly necessary, chore of establishing data bases for pit initiation times and growth rates, effects of crevice geometries, etc., must be organized before life prediction modeling related to localized corrosion processes can be attempted. Empirical correlations may be derivable from an adequate data base, but advances really depend on the further development of concepts and theories, as discussed in the first section of this chapter.

Environmentally Assisted Cracking

While stress corrosion cracking (SCC) has been recognized for more than 100 years in such phenomena as the caustic cracking of steam boilers, the atomistic processes that cause cracking are still primarily speculative. Similarly, the atomistics of hydrogen cracking, which is often initiated by corrosion-related cathodic processes, are still basically unknown. However, it is especially in this area that data from extensive short-term accelerated tests must be extrapolated to long lifetimes. Cyclic stresses that lead to corrosion fatigue or fatigue superimposed on SCC further complicate the matter.

Considerable progress has been made in modeling the effects of environment on crack growth in statically and cyclically loaded structures utilizing fracture mechanics concepts (*55*). However, in its application to corrosion, this engineering science has a number of limitations, owing to factors that compromise the fracture mechanics similitude concept. These include crack surface closure, small crack size, crack chemistry that varies with geometry, and large-scale yielding. In addition, random and variable amplitude loading effects in corrosion fatigue are not understood. Research must be directed at these problem areas. Although there have been significant crack-growth data developed over the past 5 years, particularly in the areas of offshore (marine) and nuclear environments, only the latter has been formalized as an accessible data source. More systematic tabulations of the data now widely dispersed in the literature are badly needed.

Furthermore, and perhaps more importantly, there is very little scientific information related to the atomistics or the mechanics of crack initiation and virtually none that attempts to predict how, when, or where cracking may initiate. Accordingly, research should be directed toward understanding the factors that determine the onset of SCC, hydrogen embrittlement, and corrosion fatigue, at least for important engineering combinations of alloy and environment. These activities should be closely correlated with basic studies that address chemomechanical rupture and destabilization of protective films.

As is often the case in materials science and engineering, the approach to life prediction where environmentally assisted cracking is involved must be one of "enlightened empiricism." The phenomena are so important that whatever empirical or semiquantitative lifetime prediction models can be developed must be used, even while they are being modified in the light of new knowledge and understanding.

Corrosion Data Base

Although the technical literature contains vast amounts of information on general corrosion rates, corrosion-related crack initiation and propagation rates, and localized corrosion initiation and propagation rates, there has been no real attempt to collect these data in a single compendium—e.g., in a handbook. Currently there is a small program under way at the National Bureau of Standards, jointly sponsored by the National Association of Corrosion Engineers, but because of limitations on the size of the effort, it deals primarily with thermodynamic information and cannot readily be utilized in support of life prediction.

There is thus an immediate need for the development of an accessible corrosion data base from available information. Once the data base has been established, it will be necessary to determine which data are not available and to attempt to complete the data base. It is imperative that the data that are collected and generated be available in a format that is as useful to design engineers as information that is available on other time-dependent failure phenomena (e.g., fatigue, creep, and stress rupture), possibly through the use of expert systems, as discussed in Chapter 6 of this report. It is also important that the data be available in a format that is useful in developing and testing lifetime prediction models. Ultimately, these models will be based on fundamental mechanisms and will provide the relation between accelerated tests and long-term component performance that is, overall, one of the primary goals of the corrosion science and engineering community.

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Chapter 5

ADVANCES IN STABILIZATION OF INTERFACES AND STRUCTURE

SUMMARY

The corrosion resistance of commercially available alloys has improved dramatically over the past 3 decades. A major reason for this improvement has been the development of new alloys and surface processing technologies. This has led to increased sophistication in the selection of alloys with superior corrosion resistance for particular applications. Materials producers now have strategies for control of alloy composition, morphology, and microstructure. Examples are the use of molybdenum in low-alloy steels to resist pitting and the microstructural control of titanium alloys to prevent stress corrosion cracking. Interface stability is enhanced in the first case by composition modification and in the second by manipulation of the structural processing of the alloy. Continued improvements are to be expected as these and other alloy development activities are extended, making use of the results of the research discussed in Chapter 4.

Corrosion may be important in the use of materials with unique properties, such as thermal stability, ionic conductivity, or various mechanical, electronic, optical, or magnetic characteristics. Ceramics, electronic and magnetic materials, fiber-matrix composites, and metastable materials are notable examples of these kinds of materials. This chapter examines the needs for research and technology development for specific classes of materials, including

- Protective surface phases: New processing techniques, new alloy compositions, and new capabilities for understanding these materials and their behavior have opened the way for possible improvements in corrosion resistance; work is needed to characterize the new materials and to identify parameters that determine their performance.

- Ceramics: Developments in experimental techniques and in theory are needed to explain long-term degradation of ceramics by corrosive processes, with ultimate benefit to both high- and low-technology systems where ceramics play a unique role.

- Thin films and electronic, magnetic, and optical materials: Requirements for high reliability in microelectronic and other advanced technology systems place extraordinary demands on the control of

corrosion; research directions are proposed that would provide fundamental understanding, with particular emphasis on the microscopic scale of the systems involved.

- Composite materials: Like other combinations of dissimilar materials, fiber-matrix composites may suffer from corrosive attack in specific use environments; corrosion at internal interfaces and external surfaces needs further elucidation.

- Metastable alloys: Although often exhibiting enhanced corrosion resistance compared to conventional alloys, metastable and extremely fine-grained materials usually contain interfacial regions that are susceptible to corrosive attack when consolidated into macroscopic sections; a framework is required to establish the origin of the inherent corrosion resistance of these materials and to determine the nature of their corrosion-susceptible regions.

PROTECTIVE SURFACE PHASES

Inorganic and organic coatings, physical and chemical surface modifications, and surface layers produced by liquid and vapor phase inhibitors have been used for centuries to protect materials against corrosion. The application of one or more of these protective surface phases is often the only way a substrate material can be kept from corroding in use, and an appropriate combination of substrate and surface phase frequently provides the most economical approach in structural design and fabrication. As a result, protective surface phases constitute a major commercial technology. Improvements in corrosion resistance through the use of protective surface phases, to a large extent achieved empirically in the past, have more recently been supported by advances in surface characterization and by developments in surface modification and processing (*1*,*2*). The electron microscopies and the surface-sensitive electron and x-ray spectroscopies have, with other approaches, contributed to the understanding of the mechanisms of failure in corrosion protection by improving spatial resolution in the analysis of surface phase composition and structure, especially at the substrate interface. With new processing techniques, many of them derived from developments in the electronics industry, the resistance to corrosion provided by existing protection strategies of this kind has been improved, and new strategies, utilizing new materials in the formation of protective surface phases, have been made possible.

The materials and processes used to produce protective surface phases can be grouped into several categories.

Metallic and Ceramic Coatings

Both low- and high-temperature processes can be used in the preparation of metal and ceramic coatings, although the formation of ceramics (and glasses, as well) is usually carried out at high temperatures. The low-temperature techniques (*2*) include the following processes:

- Electrodeposition and electroless deposition, by which metals and alloys can be produced. Pulsed electrodeposition and certain electroless processes can also produce metallic glasses.

- Ion plating, which involves the deposition of vapor-phase ions at electrically charged surfaces and by which metals and alloys can be produced.

- Chemical vapor deposition, which involves chemical reactions of vapor-phase species to produce metals, alloys, and chemical compounds, including ceramics.

- Evaporation and sputtering, which involve the deposition of materials and combinations of materials by physical vapor transport.

- Mechanochemical deposition, which involves grinding to sinter small metallic particles together.

- Metal cladding, which involves mechanical bonding of surface layers onto a substrate.

The high-temperature techniques (*2,3*) include the following:

- Chemical vapor deposition, as described above.

- Evaporation and sputtering, as described above.

- Pack cementation, which involves the deposition of metal by elevated-temperature chemical reaction with the volatile metal halide.

- Spray and detonation gun coating, which involves the impaction of particles melted by flame, plasma, or detonation.

- Laser-assisted spraying, which involves the impaction of particles melted by a high-power laser.

- Sol-gel coating, which involves the application of a stable dispersion of colloidal hydrous oxides or hydroxides in a liquid (the sol), the drying of this coating to give a gel, and the firing of the gel to give a ceramic or glass.

Organic Coatings

An enormous variety of organic materials can be applied to surfaces for protection against corrosion. In many cases metallic coatings are used underneath the organic coating, and in all cases the preparation of the surface prior to the application of the organic coating is important. In addition to organic components, these coatings frequently contain inorganic fillers and pigments as well as solvents that facilitate their application to surfaces. The techniques for application include brushing and spraying when solvent bases are used, electrostatic and electrochemical deposition of particulate organics that are then cured or fused, and coating with reactive organics that are subsequently cured. New compositions are continually being developed, with new polymeric components, new pigments and other additives that help inhibit degradation of the organic materials, and new solvents and new adhesives (*4*).

Physical Surface Modifications

There are two approaches to producing physical modifications of surfaces:

- Mechanical techniques, which currently involve either shot peening or shock hardening. These are mainly used to produce surface phases that contain a great deal of compressive stress, making them more resistant to stress corrosion and corrosion fatigue.

- Laser and electron beam processing, which involve rapid scanning of a surface with a high-power laser or electron beam, producing a thin molten surface layer that is rapidly solidified by heat transfer to the underlying material. Metastable surface alloys and glassy alloy surface layers, some of which show improved corrosion resistance, can be produced by these techniques.

Chemical Surface Modifications

There are two approaches to producing chemical modifications of surfaces:

- Chemical reaction, in which the surface composition is changed by reaction with a gaseous species, usually at elevated temperature. Nitriding and carbonizing are examples of this technique, which produces surface phases whose thickness is determined by diffusion.

- Ion implantation, which involves the implantation of high-energy ions into the near-surface region. This produces new metastable surface compositions, usually without causing dimensional changes, and in some cases these surface phases have improved corrosion resistance (*5*).

Surface Layers Produced by Inhibitors

There is a wide variety of materials, mainly but not exclusively organic in nature, that adsorb on or interact with surfaces to give extremely thin (in many cases monolayer) surface phases that act as barriers to corrosive environments or decrease surface reactivity. These inhibitors can be applied from liquid or vapor phase environments, but it is generally characteristic of them that a continuous supply is required to maintain their effectiveness. Some of the organic inhibitors do polymerize on surfaces, giving more permanent protection.

Impact of Corrosion

The surface phases employed for corrosion protection are themselves subject to corrosion and other types of degradation, although they are, of course, selected to withstand these forces (or to sacrifice themselves) for the periods of time during which they are intended to protect the materials to which they are applied. Metallic coatings and chemically modified surfaces undergo corrosive attack by the same processes that affect bulk metals and alloys. They can, however, be prepared with compositions and structures that cannot be matched with bulk materials, and, since they are used in small quantities, they can utilize more expensive constituents to achieve enhanced corrosion resistance. Ceramic and glass coatings are also subject to attack; specific processes affecting ceramics are discussed in a following section of this chapter. Organic coatings are typically degraded by oxidative processes, which can be accelerated by photolytic effects and by catalytic effects that involve components of the substrate. The characteristics of physically modified surfaces can change with time through diffusive relaxation of their metastable structures. All of these degradative processes are long-term. They determine the inherent capabilities of the protective surface phases in protecting substrate materials against corrosion.

In many instances, however, the protection provided to the substrate materials is determined by the existence of defects in the surface phases. Pinholes and scratches in coatings expose the substrate, which can then be corroded. This corrosion will be greatly accelerated if the coating is more noble than the substrate. Corrosion along the interface between the material and the coating can lead to delamination and more widespread attack for both inorganic and organic coatings. Defects can also be caused by unanticipated mechanical stresses that remain from processing or that are generated by differences in thermal expansivity. Stress-induced cracking is most common with coatings that are brittle or that become embrittled through aging.

Because of the widespread use of protective surface phases, their performance is critical in determining the reliability and lifetime of many structural elements important to the national economy. They find use in automobiles and other modes of transportation, in bridges and other components of the infrastructure, in buildings of all kinds, and in many specialized applications ranging from communications and electronics to the chemical process industry. The ongoing advances in the understanding and technology of protective surface phases have created further opportunities for development and application of this approach to corrosion control.

Research Opportunities

Achieving improved corrosion protection by surface phases will largely await improved fundamental understanding of the local chemistry, electrochemistry, and transport within the interfacial regions of corroding systems. The development of new techniques and theoretical concepts discussed in Chapter 4 will be important in providing the spatial and time resolutions that are needed and the theoretical foundation required for the interpretation of experimental measurements. This approach will yield the basis for improvements in processing and for the selection and development of new materials.

Specific areas open to advancement through research include studies of new protective surface phases and of failure processes.

Studies of New Protective Surface Phases

New processing techniques have made possible the preparation of surface phases with novel compositions and structures, and new developments in the understanding of corrosion phenomena are bringing into existence more systematic and fundamental approaches to corrosion protection through the inhibition of corrosion processes. Work is needed to evaluate new material systems, particularly those involving

- Metallic glass alloys with improved corrosion resistance that can be prepared by electrodeposition or electroless deposition. The combination of improved corrosion resistance that is associated with some of the glassy alloy materials and inexpensive processing technology would clearly be a valuable addition to the stock of strategies for corrosion prevention.

- Replication of highly corrosion-resistant alloys in the form of protective surface phases on less corrosion-resistant substrates. New techniques for surface coating and chemical surface modification offer many opportunities for the enhancement of corrosion resistance by this approach.

- Inhibitors whose functionality is determined by chemical design. As the mechanisms of inhibitor action are elucidated, the rationale for inhibitor selection becomes more straightforward. Further improvements in this area are of particular importance in the treatment of cooling water in the power and chemical process industries.

Studies of Failure Processes

The failures of protective surface phases are, in general, caused by defects or by what may be termed wearout. The latter is determined by such factors as the inherent characteristics of the surface phase and the interactions of the surface phase with the substrate material and with the environment in which it is used. These factors are often not well defined or understood, and thus it is difficult to select the best protective surface phase for a particular application and to determine whether a new protective surface phase offers significant advantages. Work is needed to establish and measure the parameters that determine performance and failure mechanisms for the various types of protective surface phases, among them

- The corrosion resistance of metallic and ceramic coatings, including the effects of grain boundaries and other compositional inhomogeneities

- The rates of degradation of organic coatings

- The nature and structure of the interfaces between pretreated substrates and organic coatings and their relation to corrosion protection

- The permeability of organic coatings to moisture and other atmospheric gases and the relationship between permeability and corrosion protection

- The rates of relaxation of physically modified surfaces at temperatures encountered in use

- The corrosion resistance of chemically modified surfaces

- The rates of degradation of inhibitors and the nature and impact of the products of the degradative reactions

In many cases these subjects have already been addressed, but the results of the studies that have been carried out are scattered throughout the literature. They need to be collected, evaluated, and made available for general use.

In the case of defects, the understanding of failure processes relates both to the application of protective surface phases in manufacture and to their reliability in service. Work is needed to improve the understanding of the effects of the exposure of substrate materials and substrate-surface phase interfaces in pinholes, scratches, and cracks, with specific attention devoted to such areas as

- The processes involved in corrosive attack at interfaces between substrates and inorganic and organic coatings

- The electrochemical interactions between exposed substrate materials and metallic surface phases, including chemically modified surfaces

Again, these subjects have already been addressed in many cases, but a more coherent and general approach is needed to establish the value of improved processing technologies and to provide a basis for the selection of protective surface phases for specific types of service.

This work on failure processes will provide the quantitative measures of reliability and life that are essential in the selection of corrosion protection strategies in design. These measures will also be useful in establishing needs for maintenance and replacement in varying kinds of service.

CERAMICS

Ceramics are generally considered to be inert materials that do not undergo corrosion. They are typically much more corrosion-resistant than metals, but ceramics do indeed corrode. While the corrosion of metals is an oxidative process, the corrosion of ceramics can be oxidative or reductive, and dissolution can occur without charge transfer. Ceramics have traditionally been used in severe environments because of their relative stability against corrosion. Nevertheless, corrosion of ceramics is frequently an important cost factor in metals production and other technologies.

Ceramics find application under oxidative and reductive conditions in various electrochemical systems such as high-performance batteries in the form of insulators, separators, electrodes, containers, and the electrolyte itself. The aqueous corrosion resistance of ceramics is important in a number of areas as well, including the stability of passive oxide films on metals. Serving often where they are thermodynamically unstable, ceramics work successfully in these conditions because the mass and charge transport processes that lead to degradation are appreciable only after long times or at elevated temperatures. The degradation of magnetohydrodynamic electrodes by high-temperature electrolysis is a characteristic example (*6*). In short, while ceramics are already used in a wide variety of applications in which electrochemical processes cause degradation and lifetime limitation, the corrosion of ceramics is not well appreciated, and the understanding of the processes that control it is virtually nonexistent.

Impact of Corrosion

Electrochemical Corrosion in Molten Salts, Slags, and Metals

In the production of steel, ceramics are used as refractories in blast furnaces, basic oxygen furnaces (BOFs), electric furnaces, and other instances. Most modern BOF refractories are magnesium oxide impregnated with varying amounts of carbonaceous material and are at least partially electronically conducting. The furnace contains molten metal, which is initially carbon saturated, and a slag containing CaO, MgO, Al_2O_3, SiO_2, and FeO. The MgO refractory reacts with the FeO to form low-melting solid solutions, and this leads to dissolution and degradation of the refractory. Oxygen concentration differences between the metal-slag and the slag-atmosphere interfaces supply the potential for enhanced electrochemical corrosion. Other metal-smelting operations have similar ceramics problems. Poor profitability in the pyrometallurgical industries has led to drastic reductions in research on refractories at a time when it is most needed to improve current processes and to support the new technologies needed to keep the industry competitive. In addition, with the use of electric melting of glass, ores, and steel, more direct electrochemical corrosion of ceramics is likely.

Methods for measuring corrosion of ceramics in contact with liquids at high temperature are required, as are methods to describe the thermodynamic properties of solutions and their interactions with ceramics. Solution theories are well developed for molten salt systems, where predictions of properties can often be made for complex multicomponent solutions based on data for known lower order systems (*7-9*). For complex systems such as silicates, there are promising developments for predicting properties of multicomponent systems from the better known binary systems (*10*); much work remains for extending these capabilities to corrosion research. Primary thermodynamic data on specific liquid systems and ceramic materials are needed, as are data and concepts on the rates of reactions leading to degradation.

Hot Corrosion

Ceramics can be degraded by their dissolution and reaction with molten ionic condensates, a process generally termed fluxing or hot corrosion. Thus, ceramics exposed to the cooled effluent of coal combustion or conversion systems (e.g., gasifiers) may undergo hot corrosion by molten sulfates, sulfides, or silicates. Although there have been some studies of ceramic degradation in such environments, the problems have been examined piecemeal. For coal combustion the product sulfates (and probably some silicates and sulfides) that condense will generally react chemically and/or electrochemically to dissolve ceramics of construction and thereby degrade their performance. In coal conversion processes there are probably sulfides as well as silicates involved in corrosive attack. Knowledge of the detailed mechanisms and the chemical reactions involved is scant, even though mechanisms for this type of corrosion are probably simpler than for the hot corrosion of metals. An experimental study of the kinetic and thermodynamic factors is needed to understand the dominant corrosion mechanisms and to devise control strategies (*11*).

Corrosion in Electrochemical Systems

There are a number of situations in which ceramic materials are chosen for electroactive or other properties in addition to corrosion resistance. Rigidity, strength, low expansivity, hardness, and low vapor pressure are some properties often associated with ceramics and glasses. It is convenient to consider by their function two categories of ceramic materials used in electrochemical systems: electrolytes and electrodes.

Electrolytes. Solid ceramic and glass electrolytes have utility as separators in primary and secondary storage cells as well as in chemical sensors applied both to routine analysis and to the acquisition of thermochemical and kinetic data fundamental to the study of corrosion. Zirconia and beta-alumina are two well-known electrolytes used in electrochemical cells to measure oxygen and metal activities, respectively, in a wide variety of systems.

In several applications, metal-ion-conducting solid electrolytes are subject to attack by chemically active liquid metal electrodes. Corrosive reduction reactions can occur whose effects vary from a slight coloration to massive attack. Theories to predict corrosion rates from chemical and structural principles are needed. Better experimental techniques, such as the one described by Barsoum and Tuller (*12*), for example, to measure reaction kinetics and electrochemical stability of glasses, must be employed to study these reactions.

A corrosion process apparently unique to metal-ion-conducting solid electrolytes occurs at cracks at the interface where a liquid or solid metal is discharged. Metal-filled cracks can focus ion current and sustain a sizable "Poiseuille" pressure at their tips. Above a critical average current density, the resulting stresses can extend the cracks so that the solid electrolyte fractures (*13,14*). This degradation process will no doubt be observed at some level of stimulation in any metallic ion conductor known today or yet to be discovered. From present models for the basic electromechanical effect, the critical current density is proportional to the fourth power of the critical stress intensity factor. Accordingly, more corrosion-resistant materials must be sought by applying methods of achieving greater fracture toughness. Zirconia transformation toughening, for example, is one such method.

Electrodes. Electronically conducting ceramic materials include oxides, chalcogenides, and carbides. Ceramics are candidate electrode materials in several energy conversion programs: molten carbonate fuel cells, sodium-sulfur batteries, solid oxide fuel cells, and aqueous photoelectrolytic systems. Two of these systems—sodium-sulfur batteries and photoelectrochemical systems—are discussed here to illustrate the specific needs.

In sodium-sulfur battery development, certain electrode materials—including graphite, doped Cr_2O_3, SiC, doped TiO_2, and Cr_3C_2—have been identified as having good corrosion resistance. Without exception, these ceramics are too resistive to use except in conjunction with a better conductor in a composite structure. For this and other applications there is a challenge to develop or extend ceramic forming techniques for the coating of more conductive substrates or for metal coring of thin ceramic shells.

Ceramics such as Fe_2O_3, TiO_2, $SrTiO_3$, and SiC are being considered as electrodes for photoelectrochemical applications (*15*). The stability of these compounds in the presence of the photogenerated charge carriers is clearly dependent on the electrochemical aspects of the solid-electrolyte interface. Indeed, resistance to corrosion is a crucial issue in the development of electrodes for photoelectrolytic decomposition of water. It has been difficult to find materials that have both a band gap matching the solar spectrum and thermodynamic stability against photodecomposition by electrons and holes. Several novel and different approaches have been explored, but more materials need to be explored before the true commercial potential of this type of solar converter can be assessed.

Aqueous Corrosion

In addition to being important for the stability of passive films on metals, the aqueous corrosion of ceramics is important in hydrometallurgy and in the leaching of industrial wastes such as mine tailings, fly ash, and nuclear reactor wastes, all of which lead to contamination of the environment. Ceramics are being applied to the interiors of chemical reaction vessels and smokestack scrubbers on power plants where the aqueous corrosive environment is so severe that no metal will survive for long. These ceramics are subject to aqueous corrosion.

Perhaps of even greater significance, ceramics are being developed for high-technology structural applications in severe oxidative, moist environments such as heat engines. The major ceramics of interest currently include silicon carbide (SiC), silicon nitride (Si_3N_4), and Sialon, a silicon aluminum oxynitride. Like metals, these ceramics are thermodynamically unstable in oxidizing environments. Virtually no studies have been performed with the express purpose of investigating the aqueous corrosion of nonoxide ceramics.

Another material receiving a great deal of attention for structural applications is partially stabilized zirconia. This material is of interest in that, by careful microstructure control, it exhibits very high values of fracture toughness (for ceramic materials), which are thought to be obtained through transformation toughening. This material has excellent properties, and it also may be the first ceramic material in which microstructural design was explicitly used to achieve optimum properties. Zirconia can be stabilized or partially stabilized in its high-temperature cubic modification by the addition of MgO, CaO, or Y_2O_3 in solid solution. Unfortunately, all of these stabilizers are quite soluble in both acidic and basic aqueous solutions and by themselves dissolve quite rapidly (*16*), so that degradation may occur by preferential leaching of the stabilizing compound. As their use as structural materials in severe aqueous environments increases, the corrosion behavior of ceramics will become increasingly important.

The solubilities of many oxide ceramics in simple aqueous media are reasonably well documented (*17-19*). However, it is still necessary to develop theoretical treatments that address the problems of corrosion kinetics (*20*) and the effects of surface structure (*21*), crystal structure (*22*), and electronic structure (*22,23*) on dissolution rates.

Research Opportunities

Clearly, better appreciation and understanding of the corrosion of ceramics need to be developed. These can best be achieved by research programs that develop generic understanding common to corrosion in molten salts, metals, and aqueous solutions. Specific areas in which research should be undertaken are given below. Particular attention should be given to the electrochemical aspects of this corrosion, especially as ceramics become more widely used as structural and electrochemical components in high-technology energy systems.

Thermodynamic Studies

Because ceramics are frequently used at high temperatures where equilibrium is more easily attained, thermodynamic data are particularly important in evaluating corrosion resistance and selecting ceramic materials for use. A systematic approach should be taken to fill the needs in this area, with specific attention being paid to the development of correlations and techniques that allow the thermodynamics of complex ceramic systems to be derived from those of simpler systems.

Kinetic and Mechanistic Studies

The rates of ceramic corrosion processes are often surprisingly slow, considering the thermodynamic forces that are driving them. This suggests the existence of critical inhibited steps in the overall processes, and the investigation and understanding of these would provide a basis for materials selection and development for specific circumstances. The initial stages of hydration and complexation of ions in solids are primary candidates for study (not now possible without the development of new experimental techniques).

Microstructural Studies

Desirable improvements in the mechanical properties of ceramics will certainly be based on the development of materials and processing technologies to control microstructure. New microstructural elements in ceramic materials must be studied for their effects, both beneficial and harmful, on corrosion behavior. Similarly, corrosive interactions must be studied for their effects on microstructure and the mechanical properties that derive from it. The influence of inhomogeneity, both chemical and physical, is well recognized in other areas of corrosion, and investigations of ceramics can draw on work in these areas for background relevant to the effects of microstructure. There are, however, fundamental differences between metallic and ceramic systems, particularly in the nature of the units of structure and the bonding forces, and new concepts and techniques will be needed to achieve understanding that will be useful in practical ceramic applications.

THIN FILMS AND ELECTRONIC, MAGNETIC, AND OPTICAL MATERIALS

The capabilities of the United States in data acquisition, information processing, and communications and the competitive position of the United States in international electronics markets are critically dependent on the development of new materials and device structures and their application in microelectronic and other advanced components and systems. In extending these technologies, materials are typically selected for their electronic, magnetic, or optical properties, not for their corrosion resistance or other attributes. Novel materials, such as amorphous alloys, oriented magnetically anisotropic materials, and layered two-dimensional conductors, are being studied and utilized. Furthermore, new and conventional materials, both conductors and dielectrics, are being combined in novel structures to provide devices and components with enhanced capabilities as well as multilevel interconnections.

These developments and, indeed, continued applications of current technology depend not only on materials and process research and development but also on progress in improving the reliability and reducing the cost of the final products. Understanding and preventing the corrosion phenomena that affect new materials and new combinations of materials in thin films and electronic, magnetic, and optical components are essential to achieving these goals.

In microelectronic circuitry in particular but in other advanced applications as well, high reliability is essential. Individual systems often contain very large numbers of components, all of which must function within their specification limits to keep the systems operational. Thus, failure rates corresponding to a few tens of failures in a billion operating hours are often required, even where duplex system designs are used to provide functional redundancy.

A number of inherent materials problems affecting reliability, such as electromigration of conductor materials and diffusion of impurity ions in oxides, have been addressed and are now understood well enough to be dealt with in practice. Corrosion, on the other hand, involves interactions among materials and with the local environment, which typically exhibits a variability that derives not only from variations in the operating ambient but also from the chance presence of contaminants from the materials themselves or from manufacture. Corrosion reduces reliability by degrading structures and performance; where it cannot be prevented, the use of new technological developments may be precluded.

In many cases, corrosion problems that affect reliability can be overcome without a full understanding of the phenomena involved, although generally not without an increase in cost. This approach is at present taken to a considerable extent in the packaging of microelectronic circuitry, where protective coatings and encapsulating materials may be empirically selected on the basis of general accelerated tests and where the highest reliability is usually achieved by isolation from the environment in hermetically sealed packages. For integrated circuits, packaging costs may range from 15 to more than 50 percent of the total cost. This expenditure may assure protection against 85°C, 85 percent relative humidity tests but not necessarily against conditions encountered in long-term exposure under normal use conditions. Other advanced components, such as thin-film structures for magnetic recording and electro-optic devices with light-transmitting interfaces, are more difficult to package and protect against corrosive environmental interactions because only thin protective coatings are compatible with the intended function. In these cases, elaborate and expensive approaches may be required to provide environmental isolation.

Impact of Corrosion

The fundamental corrosion processes and phenomena affecting thin films and other geometries involving new electronic, magnetic, and optical materials include most of those encountered in classical corrosion. Galvanic corrosion may occur where dissimilar materials are joined, as with gold wire bonds to aluminum or aluminum alloy conductors in integrated circuits; oxidation may take place where active metals are used, as in magnetic alloys and semiconductor devices themselves; and electrolytic corrosion may occur where potentials are applied between conductors, either across surfaces or through dielectrics.

There are several factors that often distinguish the corrosion behavior observed from that encountered in more classical cases. Perhaps most important, the physical scales involved in many of these systems are small, with dimensions measured in micrometers and fractions of micrometers for both conductors and dielectrics. One consequence is that the amount of corrosion that can cause problems is correspondingly small, particularly if the corrosion is localized. For example, a change of only a fraction of a micrometer in a conductor cross section not only changes the resistance of the conductor but also may increase the current density in the conductor to the point where electromigration becomes a problem. In thin films of magnetic and other materials, surface and grain boundary processes may result in compositional changes that affect functioning because the distances over which diffusional transport is effective are comparable to the thicknesses of the films. With thin dielectrics, electrical properties may be altered significantly by small amounts of corrosion products that dissolve in or are transported into or across the dielectric materials.

An additional consequence of small physical scale is that high electric fields appear across the surfaces and in the bulk of dielectrics. Design rules may allow fields that exceed 10,000 V/cm, which is far in excess of the values that are normally encountered in electrolytic corrosion processes, even though the potential differences may be comparable. In general, the potentials that are applied in microelectronic circuits are sufficient to carry out most electrochemical processes, making it necessary that electrolytic corrosion be prevented by nobility, by passivity, by the elimination of reactant species, or by the prevention of electrolytic transport.

Electrolytic phenomena also occur under somewhat different circumstances than are normally encountered. The electrolytes that form on surfaces with significant levels of ionic contaminants—say, by the adsorption of water—are likely to be highly concentrated, whereas the electrolytes that result from the presence of low levels of ionic contaminants on surfaces or in dielectric materials or simply from the adsorption of water or some other weakly dissociating species on surfaces are likely to be highly dilute. The transport processes in these two cases are expected to be very different. The latter may allow charge separation over significant distances, changing the expected potential distributions in the structure. In metal-oxide-semiconductor (MOS) and other microelectronic devices, these redistributed potentials can affect electrical performance; net charge concentrations of less than 10^{12} ions (charges)/cm^2 can be important.

Thus, the differences between the corrosion processes that affect thin films and those that affect bulk materials lie in the circumstances under which these processes occur. Conditions often fall outside the range normally encountered, and applications are often critically sensitive to corrosion. These circumstances have not been widely explored in corrosion research, although corrosion phenomena and their impact on reliability have been studied extensively by those concerned with the design, fabrication, and use of microelectronic components and systems (*24-27*).

Research Opportunities

It is almost axiomatic that the corrosion behavior of any new material or new combination of materials must be evaluated before it is put to use and that, if any corrosion problems are found, some means of prevention must be developed. The discussion here therefore focuses selectively on those aspects of the corrosion of thin films and new electronic, magnetic, and optical materials and structures that are unique to their applications in current and future technology. These derive primarily from the importance of effects involving small physical scale.

Microelectronic Circuitry

Research is needed on electrolytic corrosion processes involving conductors and insulating surfaces in microelectronic circuitry. Aluminum and aluminum alloy conductors and silicon dioxide, silicon nitride, and polymer surfaces are of immediate concern, but new conductor materials, among them the refractory metals molybdenum, tantalum, titanium, and tungsten and their silicides, and the insulating coatings that will be used to protect such semiconductors as gallium arsenide, indium phosphide, and mercury cadmium telluride require study for future applications. Research should be aimed at understanding

- The detailed nature of the surfaces—their compositions, their interactions with ambient species such as water, and the dependence of these on temperatures

- The behavior of ionic species on these surfaces—the mobilities of the ions and their dependence on concentrations, field strength, ambient conditions, and temperature

- The nature of the anodic and cathodic processes that occur at conductors in contact with the electrolytes present on insulating surfaces—the rates of corrosive attack as a function of potential and temperature, the extent of passivation (if any), and the species produced

- The effects of grain size and structure on the electrolytic attack of conductors

Conductors and Dielectrics

Research is needed on corrosion phenomena involving conductors and organic polymer dielectrics, both those used in packaging, such as epoxies and silicones, and those used in multilevel interconnection systems, such as polyimides. Research should be aimed at understanding

- The solubility and transport of ions and ambient species such as water and oxygen in these polymers—diffusivities and ionic mobilities and their dependence on concentration, field strength, ambient conditions, and temperature

- Anodic and cathodic processes occurring at conductors in contact with dielectrics—the effects of potential, temperature, and ambient conditions on the rates of attack, and the dependence of the species produced from both the conductor and the dielectric on these parameters

- The chemical reactions, both degradative and passivating, that occur at interfaces between conductors and dielectrics—the effects of oxygen, other ambient species, and temperature on the rates and products of reaction

- The chemical reactions that occur within dielectrics as a result of interactions involving species that are produced at the dielectric surface and diffuse to the interior—the effects of temperature and the effects of reaction on dielectric and mechanical properties

Thin Films

Research is needed on the corrosion processes that occur in thin films of materials that contain species that can react with the local ambient, among these the amorphous and oriented crystalline films used and considered for use in magnetic recording. Research should be aimed at understanding

- The detailed nature of the corrosion processes—the mechanisms of the processes and their dependence on temperature and ambient conditions

- The transport processes involved in the corrosion—the diffusive motion of species in grain boundaries, in amorphous regions, and in corrosion products

- The nature of the corrosion products, particularly in the early stages of reactions—the effects of temperature and ambient conditions, the extent of passivation by the corrosion products, and the possibility of inducing passivity by exposure to specific temperatures and ambients

- The interactions, both chemical and mechanical, with the substrates on which the films are supported—the effects of stress, from film deposition or corrosion, on the subsequent corrosion behavior of the films

The understanding gained from the corrosion research outlined here as well as studies of a similar nature can be expected to open avenues for the development of effective and economical methods of corrosion prevention, thus leading to increased reliability and reduced cost. More specifically, understanding the nature of surfaces across which electrolytic transport occurs provides a basis for exploring methods of chemical and physical surface modification that will reduce surface conductivity, while understanding the electrolytic processes that occur at conductors on such surfaces directs attention to the development of materials and coatings that will resist corrosion in these circumstances. Furthermore, understanding the nature of the surfaces that support electrolytic transport opens opportunities for improved packaging and multilevel structures through the development of materials and application processes that control conditions at this critical dielectric-to-dielectric interface at the surface of the device.

Understanding the corrosion-related processes occurring within organic polymer dielectrics and at their interfaces with conductors provides a basis for establishing the present reliability of the multilevel interconnection systems that are essential to economical advanced applications of electronic technology. This understanding, in the longer term, provides a needed basis for the development and selection of the materials and protective coatings to be used in these structures.

Understanding the corrosion processes occurring in thin films of new materials establishes requirements on protective coatings and on the materials themselves that must be met if reliable performance is to be achieved. At the same time, this understanding can quantify what can be achieved within the restrictions imposed by specific applications that do not permit appreciable physical separation from the ambient. This understanding is likely to disclose situations requiring novel approaches to corrosion prevention and thereby stimulate general progress in this area.

COMPOSITE MATERIALS

Composite materials consisting of ductile matrices surrounding strong but brittle fibers are being used in aerospace, transportation, and military applications for their high-strength, lightweight properties. These materials are fabricated by first forming the fibers and then casting the matrix material around them or hot-pressing the matrix from foils or powders. These new materials bring with them a different array of corrosion problems. Several composite materials and their corrosion problems in chloride-containing environments are reviewed here. Such exposures are characteristic of marine environments and serve as well to test corrosion resistance in other situations where these materials are used. The composites discussed have corrosion behavior that seriously limits their potential applications. Other composites not listed do not have similar problems because the fiber and matrix are more inert both separately and together. All structural composites have other limitations related to processing and manufacturing that significantly limit their use on a larger scale, but these issues will not be considered further here.

Impact of Corrosion

Boron-Aluminum Composites

Sedriks et al. (*28*) reported that there was increased anodic corrosion in aqueous chloride solutions at the interface between the aluminum matrix and the boron fibers but that it was not due to galvanic effects between the boron and the aluminum. Evans and Braddick (*29*) reported that this corrosion is confined to the exterior surface. Pohlman (*30*) found that the increased corrosion was due to the formation of a brittle aluminum boride intermetallic between the aluminum matrix and the boron fiber. The aluminum boride acts as a cathode, causes galvanic attack of the aluminum matrix, and also forms voids due to volume contraction. One solution is to coat the boron fibers with SiC to isolate the boron from the matrix. Metzger and Fishman (*31*) report that SiC-coated boron fibers are now commercially available.

Graphite-Aluminum Composites

Graphite-aluminum composites show poor corrosion resistance in marine environments. Evans and Braddick (*29*) reported that the corrosion penetrates to the subsurface layers, causing eventual swelling of the composite. Corrosion was found to initiate at the exposed ends of the graphite fibers. Batrakov et al. (*32*) also observed swelling of the composite. Aylor et al. (*33*) showed that anodizing the surface offered good protection in marine environments. They found that electroless nickel plating accelerated corrosion because the unavoidable flaws in the nickel coatings led to severe galvanic attack of the aluminum, with the nickel acting as the cathode. Czyrklis (*34*) reported that the corrosion of graphite-aluminum composites was due to the galvanic action between the fibers and the matrix, with preferential attack parallel to the fibers. Aylor and Moran (*35*) reported that the graphite does not cause galvanic attack but rather diffuses into the aluminum during fabrication and decreases the protectiveness of the surface film near the fibers. Some type of surface protection of the exposed ends of the graphite fibers is recommended by all investigators.

Alumina-Aluminum Composites

Early reports indicated that the Al_2O_3-Al composite was selectively attacked at the interface between the aluminum matrix and the fiber, but Metzger and Fishman (*31*) report that there is no serious corrosion problem with this composite. The problem of getting the aluminum to wet the Al_2O_3-Al can be overcome by adding lithium to the matrix. A compound of $Li_2O \cdot 5\ Al_2O_3$ forms on the fiber and aids bonding to the matrix.

Silicon Carbide-Aluminum Composites

Trzaskoma et al. (*36*) reported that SiC-6061 (aluminum alloy) and SiC-5456 showed corrosion characteristics in marine environments similar to those of alloys 6061 and 5456, respectively. SiC-2024 showed greater pitting than 2024. SiC-6061 exhibited a greater pit density but smaller and shallower defects than conventional 6061. They recommended anodizing to seal the surfaces, in agreement with the findings of Aylor and Moran (*35*) for SiC-6061.

Graphite-Magnesium Composites

Czyrklis (*34*) reported that graphite-magnesium composites suffer from galvanic attack and also that $Mg_{17}Al_{12}$ particles formed during processing serve as active corrosion sites.

Graphite-Epoxy Composites

Miska (*37*) reported on the problem of galvanic corrosion of metals caused by contact with graphite-epoxy composites. Graphite is conductive and very noble relative to most metals. Aluminum rivets installed in graphite epoxy composites are completely corroded after about 500 hours of exposure to 5 percent salt spray (*37*). The Air Force prohibits the use of cadmium-plated steel fasteners with graphite-epoxy panels simply because of galvanic corrosion and instead recommends the use of Ti-6Al-4V in fasteners because it shows no tendency for galvanic corrosion. Another solution is electrical isolation of the graphite with a layer of fiberglass-epoxy between the graphite-epoxy and any metal (*37*).

Research Opportunities

A general summary of the corrosion problems encountered with metal matrix composites given by Metzger and Fishman (*31*) cited three specific areas of concern: galvanic corrosion between the fiber and the matrix; selective corrosion at the interface due to new phases forming between the fiber and the matrix; and matrix defects between the fiber and the matrix providing fissures that act as pathways for corrosion. To this list should be added the possible interactions between composites and other materials in the structure.

One general but often complicated solution to the problem of the corrosion of composite materials is protection of the surfaces so that fiber ends are not exposed to the environment. In some cases, protective films on the fiber surfaces can be used to prevent attack, and it may also be possible to incorporate inhibitors into the fiber-matrix interface during processing and thus limit corrosion. The development of such solutions requires a sound understanding of basic corrosion processes, which would be elucidated by research activities in the following areas.

Studies of Interfacial Composition and Corrosion

Interfacial reactions between matrix and fiber materials can result in products that are protective against corrosion because they isolate the fibers from the matrix. As a matter of concern, however, the products of interfacial reactions can also enhance corrosion, either by acting as cathodes for galvanic attack of the surrounding structure or by being sufficiently active that they themselves are attacked. Work is needed to identify these species and to determine their corrosion behavior, using a systematic approach that allows matrix-fiber material interactions to be investigated prior to the fabrication of structural components. These studies will require the use of analytical techniques suitable for examining thin interfacial regions as well as experimental procedures appropriate for the investigation of localized corrosion. Both of these are developing areas that are discussed elsewhere in this report. The results of this work will provide a basis for materials evaluation and selection for the development of new corrosion-resistant composite materials.

Studies of Protective Coatings for Matrix-Fiber Galvanic Couples

Problems with the corrosion of composite materials are generally associated with the exposure of the ends of the fibers. When the fibers and the matrix have significantly different electrochemical characteristics, galvanic corrosion can occur, driven by the dissimilar material couples at the surface. The dissimilarity in the materials makes the application of protective coatings difficult because the chemistry or electrochemistry that is appropriate for one material is seldom appropriate for the other. The result is typically the production of porous or nonadherent electrodeposits or organic coatings, and any of these defects may actually enhance corrosion. Work is needed to examine the processes available for the application of protective coatings to these surfaces, with attention focused on surface pretreatments and, for electroplating, the initial stages of deposition. The results of these studies will support the development of protection technologies, both for composite materials and for other material systems in which galvanic coupling causes problems.

The development of corrosion-resistant fiber-matrix composites will facilitate the production and broader application of light materials (mainly for transportation and defense) that have exceptional mechanical properties without the corrosion problems that currently limit or complicate use.

METASTABLE ALLOYS

In many alloy systems, liquid phases may be rapidly quenched to produce metastable (nonequilibrium) solids, which may be either glassy or microcrystalline. Because the cooling rates required in the quenching from the liquid are high (10^5 to 10^9 K/sec), the solids produced by this rapid solidification processing (RSP) must be small in at least one dimension and are typically ribbons, powders, or flakes 5 to 50 μm thick. Metastable solids can also be prepared by electroless plating, by diffusional reaction processes, and by consolidation of RSP strip or powder. The latter approaches enable thick sections of metastable materials to be made. Surface layers of metastable materials can be formed by such techniques as ion implantation, sputtering, and laser surface melting.

The production of metastable solids by RSP holds promise for materials that are unattainable through conventional technology. The potential for supersaturation of beneficial alloying elements (extended solid solubility) and extraordinary microstructural control leads to the possibility of developing through RSP new families of alloys tailored to meet the demands of contemporary and advanced technologies.

Rapidly quenched materials may be used in the as-cast form as, for example, are ribbons of metallic glasses in magnetic applications. For applications requiring macroscopically larger sections of materials, the rapidly solidified materials must be consolidated without destroying their unique constitutional features and without compromising the properties of the consolidated product. In the consolidation, strips, particles, or flakes of the quenched materials are compacted together and hot-extruded into the form of sections of rather larger size. The alloys processed in this way are not amorphous but have grain sizes on the order of a micrometer. Because of the rapid solidification, they are chemically more homogeneous than conventional wrought alloys of the same composition. Such materials can be produced in large sections and are often remarkably stable with regard to grain growth. These materials are often relatively corrosion-resistant, but not as corrosion-resistant as the corresponding glassy alloys. The corrosion resistance of rapidly solidified alloys has received much recent attention (*38-40*) and the results are summarized in the following.

Impact of Corrosion

Glassy metal alloys have been known to the materials science community for more than 2 decades, but it is only recently that the rapid-quenching techniques have been developed to produce glassy alloys economically for commercial use. These alloys are structurally and chemically metastable. Some are remarkably strong, some are soft ferromagnets, some are catalytically active, and many are chemically inert. However, in shapes that are small in at least one dimension and therefore have high surface-to-volume ratios, the question of environmental stability or corrosion resistance in service becomes extremely important, since even a very small corrosion rate may lead to failure. Likewise, localized attack (pitting) that leaves the majority of the surface unaffected may lead to rapid local perforation. Moreover, if such materials are devitrified, they may lose their corrosion resistance as well as other useful properties.

Consolidation provides a way of achieving more macroscopic sections and more possibilities for commercial use. One of the most troublesome and least documented aspects of consolidation practice, with corrosion consequences, is the presence of features known as prior particle boundaries in the consolidated RSP alloys. These greatly affect properties. Prior particle boundaries are likely to have been surface films that were generated during solidification or developed during subsequent handling and consolidation. The exact nature of these interfaces—their origin, chemistry, and control—is uncertain.

As an example of the problems associated with prior particle boundaries, it is worth noting that transgranular stress corrosion cracking occurs in consolidated RSP austenitic alloys to a lesser degree than in conventionally processed austenitic stainless steels upon exposure to hot chloride-containing aqueous environments (*40*). In the RSP case, however, extensive delamination also occurs along foil boundaries; in the absence of corrosive media, such delamination does not occur. There is reason to be optimistic about the improvements observed in the SCC behavior of consolidated RSP austenitic alloys, since these materials suffer a smaller ductility loss than conventionally processed alloys. At this stage, however, it is important that much of the intrinsic behavior of these alloys has not yet been examined because prior particle boundaries appear to compromise their properties. Prior particle boundaries affect the behavior of other consolidated alloys in much the same way. On the other hand, there may be applications, perhaps at high temperatures, where a distributed contaminant may be used to advantage if its distribution is controlled.

Research Opportunities

The corrosion resistance of glassy and microcrystalline metastable alloys is often greater than that of their crystalline counterparts. This improvement is generally associated with their chemical composition and homogeneity, but other factors may well play a role. As new metastable alloys are developed, their resistance to corrosion must be evaluated before they can be considered for use, just as with more conventional metals and alloys.

With consolidated RSP materials, prior particle boundaries—emphasized by surface films developed either during cooling of liquid or solid or during subsequent consolidation using currently available practice—are widely considered to compromise chemical and mechanical properties. Hence, the development of particulate handling and consolidation technology capable of minimizing or eliminating prior particle boundary effects is an important priority. Without this development, it will not be possible to take full advantage of the inherent corrosion resistance of the unconsolidated materials, nor will it be possible to take advantage of any of the other desirable characteristics of these materials.

Specific areas of research that could be profitably pursued include the following:

- Investigations of the corrosion behavior of glassy and microcrystalline metastable alloys. Work is needed to identify and understand the factors responsible for any enhancements in the corrosion resistance of these materials with respect to their macrocrystalline (wrought) counterparts. It is to be expected that the absence of phase separation in the case of the glassy alloys and the microscopic scale of the phases formed in the microcrystalline alloys will be important, but the chemistry and electrochemistry of corrosion processes—for example, the nature of anodic dissolution and the formation of passive films—may also be significant, particularly in situations where supersaturation of alloying components has been achieved. Because much of the technological interest in these alloys derives from their improved mechanical properties, studies of the effects of mechanical stress on corrosion behavior will be especialy important in determining the overall utility of these materials and in selecting those whose commercial development should be encouraged.

- Studies of prior particle boundaries. Consolidation techniques for producing thick sections of metastable alloy materials also produce prior particle boundaries, which are often subject to selective corrosive attack. Work is needed to determine the composition and structure of these boundaries and to establish the mechanisms by which they are formed and attacked. To the extent that the boundaries consist of residues of surface films formed prior to or during consolidation, the results of these studies will be useful in selecting processing modifications to minimize or eliminate them. On the other hand, to the extent that the boundaries and their behavior in corrosion are found to be inherent to the interfacial regions in these microcrystalline materials and thus resemble the more familiar grain boundary regions of bulk alloys, the results of these studies will provide a basis for modifications in alloy composition to minimize boundary effects. Because of the extremely small scale of prior particle boundaries, these studies will need to draw on experimental techniques with very high spatial resolution and sensitivity that utilize developments discussed elsewhere in this report.

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Chapter 6

DISSEMINATION OF CORROSION INFORMATION

SUMMARY

As discussed in the previous two chapters, the prevention and control of corrosion depend on the continued development and application of principles of corrosion science and engineering in systems design. This chapter focuses on three additional issues—education in corrosion science and engineering, technology transfer, and expert systems for corrosion engineering. Education must be addressed at several levels: in the curricula of design engineers, in the undergraduate and graduate education of those who enter the field of corrosion science and engineering, and in the continuing education of all those concerned with corrosion.

Transfer of corrosion technology requires a systems approach that provides both the methodology and the mechanisms necessary to translate knowledge into practice. This approach must consider the multidisciplinary nature of the subject matter, the wide range of materials systems and use conditions encountered, and the wide variations in background and expertise of those to whom the technology is being transferred. Computer-based expert systems clearly offer the opportunity to enhance technology transfer. Several such systems are currently being developed, and evaluations of this approach and its limitations are needed.

EDUCATION IN CORROSION SCIENCE AND ENGINEERING

Education of Corrosion Engineers

Improved education in corrosion science and engineering becomes increasingly important as key programs such as the minerals thermochemistry program of the Bureau of Mines and industrial R&D facilities are closed or directed away from development of corrosion-resistant alloys and associated data bases. There is an obvious need for engineers who understand the processes involved in corrosion and who are able to apply that understanding to the development of designs and processes for the control and prevention of corrosion. This need is being superficially addressed at a large number of universities that offer formal under- graduate and graduate courses in corrosion science and engineering. A recent survey conducted by the National Association of Corrosion Engineers (*1*) indicates that the extent of this training may be a single course in corrosion or that corrosion is covered as part of an introductory materials course. This situation is reflected in the narrow training of present corrosion scientists and practitioners—in either metallurgy or electrochemistry—and without the mathematical modeling taught in chemical engineering curricula. In general, at the bachelor's level, a "corrosion engineering" degree does not exist, and few universities offer two or more courses in corrosion or corrosion courses involving laboratory exercises (*1*).

Considering that most students who take corrosion courses are majoring in materials science or engineering, the opportunity for increased exposure to corrosion courses is limited. The recent trend in many "traditional metallurgy" curricula to encompass "materials science and engineering" will further lessen student exposure to corrosion courses. As departments become more "materials" oriented, the students are required to become familiar with the processing, structure, and properties of not only metals but also ceramics, polymers, composites, and electronic or semiconducting materials. As a result, the amount of time in a curriculum that can be devoted to a specialized area such as corrosion becomes even more limited. Furthermore, there are few departments of sufficient size that an undergraduate may specialize in a corrosion option. Either there are insufficient faculty to teach courses or an insufficient number of students taking them to justify additional courses.

From a pragmatic viewpoint, specialization in corrosion science and engineering in universities must begin at the graduate level. Corrosion science and engineering programs specifically aimed at educating specialists at the graduate level (M.S. and Ph.D.) are, however, in place at only a small number of universities, primarily in metallurgy or materials science and engineering departments. Even where such programs exist in the United States, there are only a few courses available that deal with advanced corrosion science and engineering topics. At present, most U.S. corrosion courses, even at advanced levels, neglect both nonmetals and extreme environments. With the increasing use and importance in modern technology of ceramics, polymers, composites, and electronic materials and their inclusion into materials engineering and science curricula, it is increasingly important to include the corrosion behavior of these materials in education programs as well. The area of corrosion of materials in extreme environments (high temperature, pressure, and corrosivity) is becoming increasingly important, especially in new energy-generating technologies.

The panel concluded that some universities should develop extensive corrosion programs. For example, the University of Manchester in the United Kingdom offers more than 20 postgraduate courses in corrosion. The strengths of these programs should be a factor in the block funding discussed later in this section.

Almost none of the U.S. programs in existence require interaction with other related disciplines, and few appear to encourage this. Yet corrosion, typical of many areas of materials science and engineering, is a highly multidisciplinary endeavor, requiring interactions among the fields of chemistry, physics, mechanics, chemical engineering, and materials. A likely result of such interactions would be the development of new experimental techniques and adaptation of existing ones used in other fields for corrosion studies. Also, there is a clear need for more and better textbooks, both elementary and advanced, that emphasize the multidisciplinary nature of corrosion science and engineering.

The education of engineers at the bachelor's level is deemed inadequate with respect to corrosion; it is frequently limited to a single course in a materials curriculum. Efforts should be made to include more laboratory experience in corrosion in conjunction with lecture courses at this level. Only in very large departments that have sufficient faculty and students interested in corrosion will a "materials corrosion option" become a reality. Similarly, there are too few in-depth graduate programs in corrosion as well. The lack at both the undergraduate and graduate levels of sufficiently large programs suggests that group research support in corrosion may be necessary to bring together sufficient faculty and students to generate in-depth educational programs in corrosion engineering.

Education of Design Engineers

It is particularly important that students in disciplines such as aeronautical, mechanical, chemical, electrical, nuclear, and civil engineering be exposed to at least an introduction to corrosion principles and the selection of materials for corrosion prevention and control. This would be best accomplished at the undergraduate level in academic institutions by requiring all engineers to take at least one course on corrosion. However, as is the case in materials engineering curricula, these undergraduate programs also cover a wide variety of topics, leaving little room for additional courses. Thus, it is probably unrealistic to suggest the requirement of a course specializing in corrosion. However, a course in materials science and engineering principles with a strong emphasis on materials properties, performance, and selection should be mandatory for all design engineers. The corrosion of materials could be an important part of such a course, particularly if it were taught by the materials science or engineering department. Such a course would differ from a materials science course that emphasizes materials processing, structure, and properties. Surprisingly few such courses are required in the major engineering undergraduate programs. Where required materials courses do exist, they are frequently taught as introductory materials science courses or are taught within the given department and are narrow in scope.

Courses of this nature should be required for the accreditation of university engineering programs and should be encouraged for the licensing of professional engineers. It should be incumbent on the Accreditation Board for Engineering and Technology (ABET) to enforce course requirements in materials performance and selection, including corrosion, for all undergraduate engineering degree programs. It is recommended that, as a minimum, a basic materials course including the use of corrosion principles for design applications be required in engineering departments to qualify for accreditation at the bachelor's level. It is also recommended that licensing examinations for professional engineers include some minimum number of questions related to corrosion considerations in design. The number and types of questions required should be developed in cooperation with technical societies such as the National Association of Corrosion Engineers.

Implementing these educational, accreditation, and licensing requirements will surely reduce the incidence of failure in future designs arising from inadequate consideration of corrosion phenomena.

Continuing Education

A need also exists for continuing education of corrosion professionals in up-to-date theory as well as laboratory and field techniques related to modern corrosion science and engineering. In addition, there should be educational opportunities for design engineers to be exposed to the latest information on design for corrosion prevention and control. Currently these are provided by technical societies such as the National Association of Corrosion Engineers, The Electrochemical Society, and, to some extent, the American Society for Metals through their technical meetings and specific short courses. A number of universities also conduct short courses of 1 or 2 weeks' duration, primarily oriented toward the entry-level education of nonexperts and usually limited to the fundamentals of corrosion. Large industrial research facilities should also be considered as resources for continuing education of the engineering community, particularly of the "in-house" staff. Government and industrial support is given to such programs by allowing employees to attend. In addition, some government and industry support is available for the sponsorship of more specialized topical meetings at the advanced level for the discussion of specific topics in corrosion science and technology. The panel endorses expanding these efforts to include relatively new methods such as videotapes.

University and Federal Agency Interactions

Currently, the primary interaction between the federal government and the universities with regard to corrosion arises in the form of individual research grants or contracts for graduate and/or postdoctoral studies on specific problems. As discussed earlier, one of the problems in corrosion education is the lack of departments having a sufficient number of faculty and students to provide an in-depth curriculum in corrosion at either the undergraduate or graduate level. Furthermore, much corrosion education and research lacks cross-disciplinary interactions between materials departments and other academic departments such as chemistry and physics.

To overcome both of these problems, block funding of corrosion research should be considered by the federal agencies. Block funding of several investigators at one or more universities focusing on corrosion problems would bring together sufficient faculty and students to provide in-depth corrosion education. Such mechanisms for funding already exist within the National Science Foundation in the form of the Materials Research Laboratories and Materials Research Groups. The latter seem to be an ideal mechanism to generate a sufficiently large program with the necessary cross-disciplinary communication; it is recommended that universities that have, or have the potential of developing, a strong graduate and undergraduate program in corrosion of materials apply for such funding.

TECHNOLOGY TRANSFER

Technology transfer of corrosion control is directly related to education and implies greater coordination between scientists and practicing engineers. Application of corrosion science and engineering principles is essential to (a) the selection of materials and designs to resist corrosion, (b) the choice of protection technologies to stabilize material systems against corrosion, and (c) the determination of requirements for maintenance and repair associated with corrosion. The information base for these purposes is generated by several fairly distinct groups of workers in the field of corrosion and disseminated to its users by several different routes. The process of transferring this information must accommodate the large range of possible materials systems and use conditions, the numerous possible combinations and interactions of chemical and physical phenomena, and the wide variations in user background and orientation.

Interactions Among Educators, Researchers, and Practitioners

Corrosion professionals fall into three main groups: university professors, government and industrial laboratory researchers, and practicing corrosion engineers and scientists. Individuals whose principal training is not in corrosion but in other areas of science and engineering may become involved with the field of corrosion because of its wide-ranging, multidisciplinary nature.

In universities, corrosion research and education is led by professors in metallurgy or materials departments who may have little experience in government or industrial laboratories or as practicing corrosion engineers. Corrosion research usually consists of individual projects involving graduate and postgraduate students focused on some fundamental aspect of corrosion science. The results of the work are presented in technical publications and in contract reports. University professors may share their expertise in corrosion by consulting with government or industrial laboratories and, more rarely, with those who practice corrosion engineering.

University education in corrosion produces graduates who may become researchers or practicing corrosion engineers. In government and industrial laboratories, corrosion research and development are usually carried out by individuals with backgrounds similar to those in universities. Depending on the needs of the organization, the work in corrosion is frequently more application-oriented than that in the university, and there is more likelihood of its involving multidisciplinary teams and systems analysis. Results from this type of research often appear in technical journals and contract reports.

In contrast, the practice of corrosion engineering occurs in an economic environment in which important decisions on corrosion prevention and control must be made and complex corrosion problems must be solved. As a result, practicing corrosion engineers have developed rules of thumb and empirical procedures to assist them in dealing with complex corrosion systems, which may or may not be based on available corrosion science data. Information on successful practice and on solutions to specific problems is disseminated through publications that emphasize this more empirical, rule-based approach, often with an interpretation that is descriptive rather than quantitative and analytical. In industrial laboratories, systems approaches to more complex corrosion problems frequently involve proprietary information and are not made available in the open literature. The extent to which internal consultation on corrosion problems occurs in industrial organizations varies widely; strengthening communication between scientists and engineers within single technology sectors is urgently needed.

Barriers to Information Exchange

The technical literature reporting laboratory research has little overlap with the technical literature reporting practical solutions to corrosion problems. As a result, there is a significant lack of communication between laboratory research and problem-solving. Review papers, up-to-date books, and handbooks help reduce this lack of communication. Unfortunately, the availability of review papers, books, and handbooks on corrosion lags far behind the need.

However, the major factor that inhibits effective transfer of corrosion information and technology from fundamental corrosion scientists to practicing corrosion engineers is the lack of an approach that applies basic understanding to engineering problems. The complexity of these problems requires (a) tapping knowledge accumulated in other fields such as chemistry, physics, and materials science and (b) using new modeling techniques, available data bases, and expert systems. These will ultimately provide the basis for the needed application of fundamental research to practical corrosion prevention and control.

For those whose practice of corrosion engineering is peripheral but essential to their main work, the effective transfer of corrosion information and technology often involves more specific needs. In particular, designers of machines and structures must select materials that economically meet the functional requirements of a design while providing appropriate resistance to corrosion. The designer's needs may be met by handbooks, by institutional design manuals, or by consultation with experienced corrosion engineers. Too often these resources are inadequate or are neglected until there are corrosion problems or early failures in use. There is a need for education of design engineers in corrosion prevention and control, as discussed earlier. There is also a need for readily available corrosion information at a level that can be used by a design engineer who is not a corrosion specialist. Computer-based expert systems offer much promise in fulfilling this latter need. Transfer of information to those concerned with corrosion preventive maintenance might also be accomplished in this way.

Recommendations

Implementation of the following recommendations will improve the transfer of information on corrosion science and practice to the user. A number of them are related to matters discussed elsewhere in this report, but here the emphasis is on technology transfer.

■ A systems approach to practical corrosion engineering should be developed, utilizing the developing techniques of modeling and computational analysis discussed in Chapter 4. The focus here, however, should be on integrating the elements required to translate knowledge into improved practice in corrosion engineering. This will involve both scientific and engineering capabilities of specific companies and industries.

- A systems-oriented text on corrosion is needed in support of the systems approach to corrosion engineering. There is an excellent text on electrochemical systems (*2*), but the most quantitative text on corrosion is basically a text on corrosion science, which has only recently been updated and translated into English (*3*).

- Communication between corrosion researchers and practitioners should be encouraged as an extension of the more individual aspects of education discussed earlier in this chapter. Continuing education, interpretive and summary talks at technical meetings, and reviews in the technical literature of both groups could provide a start in ensuring the dissemination of new ideas and interpretations and in making researchers aware of needs and opportunities for new research.

- New methods for the transfer of corrosion information and technology to users should be developed. Computer-based expert systems for corrosion engineering, discussed in the next section of this chapter, provide one method that should be examined. Widely accessible data banks of critically evaluated information on corrosion phenomena and on the chemical and physical properties of components important in corrosion systems, particularly concentrated electrolytes, would facilitate the practice of corrosion engineering as well as more fundamental work involving experimentation and modeling.

EXPERT SYSTEMS FOR CORROSION ENGINEERING

Artificial Intelligence and Corrosion Engineering

For several decades, research and development have been carried out on the subject of artificial intelligence, which can very roughly be described as the theory and practice of providing computers with some useful semblance of human intelligence. This work has focused on a wide variety of topics, among them expert systems, which are intended to connect items in a body of stored information in such a way as to provide conclusions about user-defined situations and to suggest solutions to user-defined problems.

A considerable number of applications of expert systems have been developed to run on mainframes and minicomputers. Recently, software that supports expert systems has been marketed for personal computers (*4*), and while these products now lack the power available in programs that run on larger and faster computers, their capabilities can be expected to increase in response to the needs of the very sizable number of prospective users.

The techniques of artificial intelligence offer opportunities for significantly increased corrosion control through application of corrosion engineering to design. Because designers rarely have much training in corrosion engineering, they must therefore depend on the application of standard practices, on knowledge gained from experience, and on access to a quite limited number of corrosion engineering experts for guidance in their designs. This situation perpetuates the major cost of metallic corrosion in the United States, estimated at approximately $70 billion in 1975 (*5*). Improvements in the application of corrosion engineering in design would provide positive benefits as well. With a better knowledge of corrosion behavior, materials use can be optimized, so that the needs of a specific design are met without excessive allowances for contingencies that are unforeseen because they are not considered. With a better knowledge of corrosion behavior, designs can also be optimized, providing, for example, enhanced capabilities or reductions in size or weight by the appropriate dimensioning of materials.

An Expert Corrosion Engineering System

Corrosion engineering is based on two main components: (a) the extensive but highly dispersed knowledge base that derives from corrosion science and (b) the expertise in corrosion testing and experience that belongs to those in the somewhat ill-defined category of corrosion engineering. Ideally, artificial intelligence techniques could be used to incorporate both of these components in the stored data base of a computer and to provide answers derivable from this data base and from mathematical modeling to questions posed by a user, whether experienced or not. This ideal is currently far from being achievable, and a more practical approach appears to be that embodied in a rule-based expert system, applicable at first to a limited range of problems but capable of being expanded and ultimately developed into a system that could be integrated into an overall system for computer-aided design. Prototype systems using this approach are already being developed for marine corrosion (*6*), high-strength aluminum alloys (*7*), pressurized water nuclear reactors (*8*), and structural alloys associated with recovery and production of hydrocarbons from sour wells—i.e., those with high hydrogen sulfide content (*9*).

Rule-based expert systems, as presently constituted, typically consist of three principal components. The first is a knowledge base, which is made up of a series of "if, then" rules concerning situations and responses, usually with some measure of the certainty connecting the situation with the response. The second is an inference engine, which processes the rules following the input of a user query at the simplest level and most commonly either by matching a situation that is input with the "if" portion of a rule (forward chaining) or by matching a response that is input with the "then" portion of a rule (backward chaining). The third is a report generator, which provides the user with both an answer and an explanation of the inference process. The most important factors determining the performance of any expert system are the decisions concerning what is actually needed in the knowledge base and the understanding of how these items are in fact used by experts in arriving at conclusions. These are problems being addressed in a number of ways by work in the artificial intelligence community.

The initial scope for the development of a rule-based expert corrosion engineering system should probably be limited, with attention focused on a few selected areas of concern in which sizable amounts of data and engineering expertise already exist and where the utility and value of such a system could be most readily demonstrated. Situations in which materials individually and in pairs are exposed to relatively specific and invariant environments would be a good place to start, with consideration given to the effects of material processing, geometry, surface treatments, and assembly processes. The expert system should be capable of drawing from the user or designer an adequate description of the contemplated material use and provide an "expert" evaluation of the suitability of the application, the limitations to be considered, and, possibly, alternate materials that might be more appropriate.

The development of such systems will require expertise in corrosion engineering, both for input of the knowledge base and for validation of output. It will also require representative user involvement and, very likely, some level of expertise in the application of expert systems. There are now a number of expert system development "shells" available, including several for personal computers that are powerful enough to serve as the basis for developing expert systems to deal with such matters as the selection of materials for pressurized water reactor steam generators in nuclear energy plants (*4*). Initial expert corrosion engineering systems might well be developed satisfactorily using one of these shells, but a careful selection of software will be required if the system is to accommodate expansion to deal with a variety of complex situations.

All expert systems are limited in their capabilities by the amount and quality of information contained in the knowledge base, and one ever-present concern must be that an appropriate level of certainty be attached to rules that incorporate generalizations with regard to corrosion behavior. It is also to be expected as a limitation that there will always be questions for which an expert system can provide no adequately certain answers. This, together with the reporting of the inference process, may in fact be useful in establishing with some precision where corrosion testing or work in corrosion science is needed.

Planning and System Development

The development of a comprehensive expert corrosion engineering system is, as contemplated above, a long-range program taking place in a number of stages, and thus planning is fundamental to its ultimate success.

There are several issues to be addressed in the planning, the first of which is the need to take into account the likelihood of major advances in computer hardware and software and in telecommunications technology in the next several years. To take advantage of these advances, the development program must have some flexibility so that it is not locked into an approach that becomes outdated.

A second issue is the assignment of responsibility for coordination and management. If the work is eventually to produce a comprehensive expert corrosion engineering system, this responsibility must be long-term, and how this is best handled must be decided.

The remaining issues mainly concern the initial steps in the planning, and these can be dealt with only through fairly detailed evaluation. Considerable attention must be directed to determining who the users will be and what they want and need. Decisions must be made on how the users will access the system. Among the possibilities here are access through terminals connected by data or voice communication lines to a central time-sharing computer, access by similar means to separate time-sharing computers on each of which the system is available, and access through individual desktop computers on which the system runs. If the system is ultimately to become part of an overall system for computer-aided design, its software development will have to be open and flexible so that it will accommodate the changes necessary for its integration with the design software in the variety of approaches being used to address this subject. Finally, decisions must be made on the stages in which the system should be developed. It would appear desirable to begin with smaller segments that would later be consolidated, but it remains to be determined whether this would, in fact, shorten the time required to provide users with a useful expert system.

Coordination With Existing Programs

Successful application of an expert corrosion engineering system to the design process will depend largely on the ease of use of the system, its cost to the user, and its ability to provide needed expertise. The last of these will require inputs of data and expertise from a large number of workers and organizations.

Many of the organizations that are supported by materials suppliers, such as the International Copper Research Association, the International Lead and Zinc Research Organization, the Iron and Steel Institute, and the Tin Research Institute, have ongoing programs concerned with the collection and dissemination of information on corrosion, and the joint Corrosion Data Program of the National Association of Corrosion Engineers and the National Bureau of Standards is collecting and evaluating existing information on both the kinetics and thermodynamics of corrosion. There are, in addition, computerized data bases dealing with corrosion and, as referred to above, a number of efforts in the development of expert systems for materials selection. More generally, a cooperative national system for accessing materials property data is being developed as the National Materials Property Network (*8*). The development of an expert corrosion engineering system must be coordinated with these other activities and must, to a considerable extent, be based on their successes.

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Appendix

BIOGRAPHICAL SKETCHES OF PANEL MEMBERS

THEODORE R. BECK earned B.S., M.S., and Ph.D. degrees in chemical engineering and electrochemistry at the University of Washington. He was at DuPont, Kaiser Aluminum, American Potash and Chemical Corporation, Boeing Scientific Research Laboratories, and Flow Research, Inc., before founding Electrochemical Technology Corporation, of which he is president. He has also been a research professor in the Department of Chemical Engineering at the University of Washington. His research interests include fused salt and aqueous electrolysis; process development; batteries; fuel cells; energy conversion; corrosion; wear; and electrokinetic phenomena.

MILTON BLANDER received his B.S. degree at Brooklyn College and his Ph.D. degree in physical chemistry at Yale University. He worked at Cornell University, Oak Ridge National Laboratory, and North American Rockwell. In 1971 he joined Argonne National Laboratory, where he is a group leader. His research interests are in pyrometallurgical research, welding chemistry, the origin of meteorites, and neutron studies of high-temperature materials.

DAVID J. DUQUETTE earned his B.S. degree at the U.S. Coast Guard Academy and his Ph.D. degree in metallurgy at Massachusetts Institute of Technology. He was involved with research at MIT and at Pratt & Whitney before going to Rensselaer Polytechnic Institute, where he is now a professor of metallurgical engineering. His expertise is in corrosion science and engineering, including the affects of environment on mechanical properties of crystalline materials, as well as in fatigue and the mechanical properties of metals and alloys.

JEROME KRUGER was educated at Georgia Institute of Technology, where he received his B.S. and M.S. degrees, and at the University of Virginia, where he received his Ph.D. degree in chemistry. He worked at the Naval Research Laboratory before joining the National Bureau of Standards, where he was leader of the Corrosion and Electrodeposition Group. He is currently professor and chairman of the Materials Science and Engineering Department of the Johns Hopkins University and is a past director and a principal faculty of the Corrosion and Electrochemistry Research Laboratory at Johns Hopkins. His research interests include corrosion science and engineering, passivity, electrochemistry, and in situ techniques.

RONALD LATANISION is Director of the School of Engineering's Materials Processing Center and of the H. H. Uhlig Corrosion Laboratory at

Massachusetts Institute of Technology. He received his B.S. in metallurgy from Pennsylvania State University in 1964 and Ph.D. from Ohio State University in 1968. A member of the National Academy of Engineering, he served as a Science Advisor to the Committee on Science and Technology of the U.S. House of Representatives during a sabbatical in 1982-1983. He is author of 100 papers and books in the field of corrosion science and engineering.

DIGBY D. MACDONALD is currently Director, Chemistry Laboratory, SRI International, in Menlo Park, California. Prior to joining SRI in 1984, he served as Professor of Metallurgical Engineering and Director of the Fontana Corrosion Center at Ohio State University. He is the author or coauthor of more than 160 research papers in electrochemistry, corrosion science, thermodynamics, and reaction kinetics as well as of a book on transient techniques in electrochemistry.

PAUL C. MILNER earned his B.S. degree at Haverford College and his M.A. and Ph.D. degrees in chemistry at Princeton University. He joined AT&T Bell Laboratories in 1957, and prior to his recent retirement he headed the Electrochemical and Contamination Research Department there. His research interests are in electrochemistry, kinetics, and thermodynamics.

DENNIS W. READEY received his B.S. degree at the University of Notre Dame and his Sc.D. in ceramics at Massachusetts Institute of Technology. He was at Argonne National Laboratory and Raytheon before going to Ohio State University, where he is professor of ceramic engineering and chairman of the department. His research interests include ceramics processing, ceramics corrosion, and optical, electronic, and transport properties of ceramics.

WILLIAM H. SMYRL is Professor of Chemical Engineering and Materials Sciences and Associate Director of the Center for Corrosion Research at the University of Minnesota. He received his Ph.D. in chemistry at the University of California, Berkeley, and spent 3 years at the Boeing Scientific Research Laboratories and 11 years at Sandia National Laboratories. He joined the faculty of the University of Minnesota in 1984. His research interests are modeling of corrosion processes, in situ techniques for metal-metal oxide interface studies, digital impedance for faradaic analysis, stress corrosion cracking, polymer-metal interfaces, and electrochemical processes.

NEILL WEBER was educated at the University of Manitoba, where he received his B.S. degree, and at Rensselaer Polytechnic Institute, where he earned his Ph.D. degree in physical chemistry. He was at Mellon Institute and Ford Motor Company before joining Ceramatec, Inc., in 1985. His research interests are in glass properties, electrochemical energy storage and conversion (including applications of ceramics in such systems), and phase equilibria in oxide systems.